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Supporting Information

# Gold(I)-Catalyzed *C*-Glycosylation of Glycosyl *ortho*-Alkynylbenzoates, a Role of the Moisture Sequestered by Molecular Sieves

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# 1. General Procedures

Commercial reagents were used without further purification unless specialized. Solvents were dried and redistilled prior to use in the usual way. Thin layer chromatography (TLC) was performed on pre-coated plates of Silica GelHF254 (0.5 mm, Yantai, China). Flash column chromatography was performed on Silica Gel H (10–40 μ, Yantai, China). Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AM 400 or Bruker AM 500 spectrometer at 25 $^{o}C$. $^{1}H$ and $^{13}C$ NMR signals were calibrated to the residual proton and carbon resonance of the solvent ($CDCl_3$: $\delta_H$ = 7.26 ppm; $\delta_C$ = 77.16 ppm). Chemical shifts are recorded in δ values and *J* values were given in Hz. Mass spectra were obtained on a HP5989A or a VG Quatro mass spectrometer. High-resolution mass spectra were obtained with IonSpec 4.7 Tesla FTMS or APEXIII 7.0 TESLA FTMS.

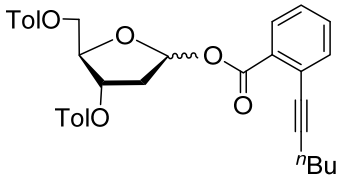
# 2. Syntheses of Substrates

Glycosyl *ortho*-hexynylbenzoates **1a**, **1b**, **1c**, and **1e**,[S1] gold(I) complex **V**,[S2] isocoumarin **VII**,[S2] gold(I) catalysts $Ph_3PAuOTf$ [S3] and $Ph_3PAuNTf_2$,[S4] and allyl silane **2b**[S5] were prepared and characterized according to the literature methods. Allyl silane **2a** and silyl enol ether **2c** are commercially available.

## 2.1. Preparation of the glycosyl *ortho*-hexynylbenzoates

*General procedure:* A solution of 2,3,5-tri-*O*-benzyl-D-arabinose (2.65 g, 6.31 mmol), *ortho*-hexynylbenzoic acid (2.10 g, 10.3 mmol), DMAP (116 mg, 0.095 mmol), EDCI (1.82 g, 9.46 mmol), and DIPEA (2.20 mL, 12.6 mmol) in dry $CH_2Cl_2$ (30 mL) was stirred for 4 h at room temperature, and was then diluted with $CH_2Cl_2$. The resulting mixture was washed with saturated $NaHCO_3$ and brine, respectively, and was then dried with $Na_2SO_4$. The solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 7:1) to provide **1f** as a colorless syrup (3.33 g, 87%, β/α = 1:6.5).

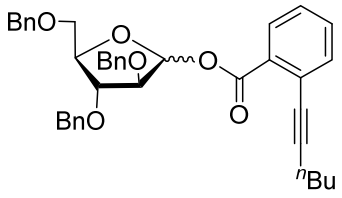
**3,5-Di-*O*-toluoyl-2-deoxy-D-ribofuranosyl *ortho*-hexynylbenzoate (1d)**




Compound **1d** was obtained (6.38 g, 78%; α/β = 1:2.5) as a colorless oil. A small portion of the anomers was separated. The β isomer: $[\alpha]_D^{29}$ = -2.2 (*c* 2.5, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.83 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.33–7.22 (m, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.75 (d, *J* = 5.2 Hz, 1H), 5.73 (dd, *J* = 9.5, 5.9 Hz, 1H), 4.68–4.60 (m, 2H), 4.55 (dd, *J* = 11.5, 5.2 Hz, 1H), 2.88 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.68–2.56 (m, 1H), 2.50 (t, *J* = 7.1 Hz, 1H), 2.42 (s, 3H), 2.35 (s, 3H), 1.67–1.55 (m, 2H), 1.59–1.45 (dq, *J* = 14.3, 7.1 Hz, 1H), 0.94 (t, *J* = 7.3 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 166.1, 165.9, 165.2, 144.2, 143.6, 134.4, 131.7, 130.9, 130.3, 129.7, 129.1, 128.9, 127.0, 126.8, 126.6, 124.8, 99.1, 96.5, 82.9, 79.2, 74.4, 64.3, 38.6, 30.7, 22.0, 21.6, 21.56, 19.4, 13.6; HR-ESIMS *m/z* calcd for $C_{34}H_{34}O_7$ $[M+Na]^+$ 577.2197, found 577.2182.

The α isomer: $[\alpha]_D^{29}$ = 59.6 (*c* 2.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 5H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.25–7.10 (m, 5H), 6.76 (d, *J* = 4.8 Hz, 1H), 5.60 (d, *J* = 6.4 Hz, 1H), 4.78 (d, *J* = 2.0 Hz, 1H), 4.60 (d, *J* = 3.0 Hz, 2H), 2.81–2.60 (m, 1H), 2.56 (d, *J* = 14.8 Hz, 1H), 2.44–2.40 (m, 8H), 1.64–1.52 (m, 2H), 1.49–1.40 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 166.2, 166.1, 165.1, 144.1, 143.9, 134.4, 131.7, 131.3, 130.4, 129.8, 129.6, 129.1, 126.9, 126.8, 126.7, 125.0, 9.2, 96.6, 84.1, 79.1, 74.4, 64.1, 38.7, 30.6, 22.0, 21.6, 21.6, 19.5, 13.6; HR-ESIMS *m/z* calcd for $C_{34}H_{34}O_7$ $[M+Na]^+$ 577.2197, found 577.2221.

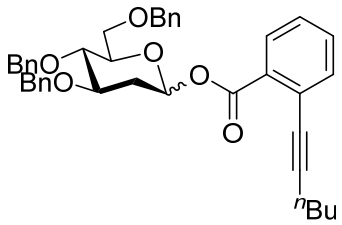
**2,3,5-Tri-*O*-benzyl-D-arabinofuranosyl *ortho*-hexynylbenzoate (1f)**



Compound **1f** was obtained (3.33 g, 87%; α/β = 6.5:1) as a colorless oil. A small portion of the anomers was separated. The β isomer: $[\alpha]_D^{25}$ = -17.3 (*c* 1.1, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.87–7.79 (m, 1H), 7.56–7.51 (m, 1H), 7.42 (td, *J* = 7.6, 1.3 Hz, 1H), 7.38–7.23 (m, 15H), 7.22–7.15 (m, 1H), 6.63 (d, *J* = 4.0 Hz, 1H), 4.80–4.49 (m, 6H), 4.39–4.20 (m, 3H), 3.66 (d, *J* = 5.2 Hz, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.67–1.55 (m, 2H), 1.56–1.42 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); $^{13}C$ NMR (100MHz, $CDCl_3$) δ 164.88, 138.3, 138.2, 137.6, 134.7, 131.9, 131.5, 130.7, 128.7, 128.61, 128.56, 128.3, 128.2, 128.0, 127.89, 127.86, 127.8, 127.3, 125.4, 96.8, 95.2, 84.3, 82.2, 81.6, 79.4, 73.6, 73.3, 72.7, 71.4, 30.9, 22.3, 19.8, 13.9; HRMS (MALDI) *m/z* calcd for $C_{39}H_{40}O_6Na$ $[M+Na]^+$ 627.2717, found 627.2732.

The α isomer: $[\alpha]_D^{25}$ = 23.0 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.39–7.18 (m, 16H), 6.55 (s, 1H), 4.76 (d, *J* = 11.9 Hz, 1H), 4.66–4.41 (m, 6H), 4.28 (s, 1H), 4.07 (d, *J* = 5.5 Hz, 1H), 3.69 (d, *J* = 5.0 Hz, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.66–1.54 (m, 2H), 1.47 (dq, *J* = 14.4, 7.1 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 164.8, 138.0, 137.6, 137.3, 134.5, 131.8, 131.0, 130.7, 128.4, 128.3, 127.88, 127.87, 127.7, 127.6, 127.0, 125.1, 101.0, 96.6, 87.0, 83.8, 83.4, 79.2, 73.4, 72.1, 72.0, 69.6, 30.7, 22.0, 19.5, 13.6; HRMS (MALDI) *m/z* calcd for $C_{39}H_{40}O_6Na$ $[M+Na]^+$ 627.2717, found 627.2740.

**3,4,6-Tri-*O*-benzyl-2-deoxy-D-glucopyranosyl *ortho*-hexynylbenzoate (1g)**

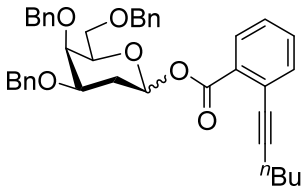



Compound **1g** was obtained (4.64 g, 80%; α/β = 1:1.5) as a colorless oil. A small portion of the anomers was separated. The β isomer: $[\alpha]_D^{22}$ = 68.6 (*c* 1.1, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.0 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.38–7.14 (m, 16H), 6.54 (dd, *J* = 1.7, 0.8 Hz, 1H), 4.96–4.46 (m, 6H), 4.06 (dd, *J* = 20.1, 8.5 Hz, 2H), 3.81 (dt, *J* = 15.9, 6.5 Hz, 2H), 3.68 (d, *J* = 10.6

Hz, 1H), 2.43 (td, *J* = 7.2, 3.2 Hz, 3H), 2.00–1.86 (m, 1H), 1.53 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.44–1.31 (m, 2H), 1.26 (s, 1H), 0.88 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.6, 138.34, 138.27, 138.0, 134.9, 131.8, 131.0, 130.6, 128.4, 128.32, 128.27, 127.92, 127.90, 127.7, 127.6, 127.1, 124.8, 96.6, 93.2, 79.7, 77.6, 76.9, 75.2, 73.8, 73.5, 71.9, 68.4, 34.5, 30.7, 22.0, 19.5, 13.6; HRMS (MALDI) *m/z* calcd for $C_{40}H_{42}O_6Na$ $[M+Na]^+$ 641.2874, found 641.2860.

The α isomer: $[\alpha]_D^{22}$ = 6.1 (*c* 0.9, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.54–7.46 (m, 1H), 7.41 (td, *J* = 7.6, 1.3 Hz, 1H), 7.37–7.15 (m, 16H), 5.94 (dd, *J* = 9.9, 2.0 Hz, 1H), 4.94–4.46 (m, 6H), 3.85–3.66 (m, 4H), 3.64–3.54 (m, 1H), 2.49 (ddd, *J* = 18.0, 9.4, 4.6 Hz, 3H), 1.91 (dd, *J* = 22.3, 11.2 Hz, 1H), 1.68–1.55 (m, 2H), 1.53–1.39 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.1, 138.2, 138.1, 138.0, 134.3, 131.9, 130.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 126.9, 125.1, 96.6, 92.6, 79.1, 78.9, 77.3, 75.8, 74.9, 73.3, 71.6, 68.5, 35.3, 30.6, 22.0, 19.4, 13.6; HRMS (MALDI) *m/z* calcd for $C_{40}H_{42}O_6Na$ $[M+Na]^+$ 641.2874, found 641.2881.

**3,4,6-Tri-*O*-benzyl-2-deoxy-D-galactopyranosyl *ortho*-hexynylbenzoate (1h)**

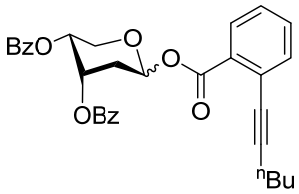



Compound **1h** was obtained (3.0 g, 80%; α/β = 1:1) as a colorless oil. A small portion of the anomers was separated. The β isomer: $[\alpha]_D^{22}$ = 43.9 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.43 (td, *J* = 7.6, 1.1 Hz, 1H), 7.39–7.19 (m, 16H), 6.54 (d, *J* = 2.1 Hz, 1H), 5.02–4.35 (m, 6H), 4.18 (dd, *J* = 7.5, 5.6 Hz, 1H), 4.11–3.98 (m, 2H), 3.68 (t, *J* = 8.5 Hz, 1H), 3.57 (dd, *J* = 9.0, 5.3 Hz, 1H), 2.52–2.33 (m, 3H), 2.17 (dd, *J* = 13.7, 3.3 Hz, 1H), 1.64–1.52 (m, 2H), 1.44 (dd, *J* = 15.0, 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.6, 138.7, 138.1, 137.9, 134.7, 131.7, 131.4, 130.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 127.1, 124.7, 96.2, 93.8, 79.6, 74.5, 74.0,

73.5, 72.7, 72.6, 70.3, 68.6, 30.7, 30.1, 22.1, 19.5, 13.6; HRMS (MALDI) *m/z* calcd for $C_{40}H_{42}O_6Na$ $[M+Na]^+$ 641.2874, found 641.2879.

The α isomer: $[\alpha]_D^{22}$ = -0.47 (*c* 1.1, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.51–7.46 (m, 1H), 7.44–7.20 (m, 17H), 5.91 (dd, *J* = 10.0, 2.4 Hz, 1H), 5.00–4.36 (m, 6H), 3.93 (s, 1H), 3.78–3.55 (m, 4H), 2.44 (t, *J* = 7.1 Hz, 2H), 2.34 (dd, *J* = 22.0, 11.9 Hz, 1H), 2.21 (dd, *J* = 8.9, 2.9 Hz, 1H), 1.63–1.52 (m, 2H), 1.45 (dq, *J* = 14.1, 7.1 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 164.2, 138.7, 138.0, 137.8, 134.3, 131.9, 130.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.73, 127.68, 127.5, 127.3, 127.0, 125.2, 96.6, 93.2, 79.1, 76.8, 74.8, 74.4, 73.5, 71.5, 70.4, 68.4, 31.5, 30.6, 22.0, 19.5, 13.6; HRMS (MALDI) *m/z* calcd for $C_{40}H_{42}O_6Na$ $[M+Na]^+$ 641.2874, found 641.2884.

**3,4-Di-*O*-benzoyl-2-deoxy-D-ribopyranosyl *ortho*-hexynylbenzoate (1i)**

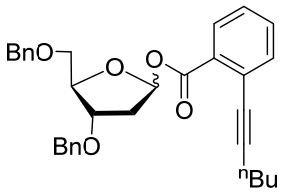



Compound **1i** was obtained (2.06 g, 90%; α/β = 3.4:1) as a colorless oil. A portion of the anomers was separated. The β isomer: $[\alpha]_D^{22}$ = 30.9 (*c* 1.3, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.98 (t, *J* = 7.6 Hz, 4H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.52 (dt, *J* = 15.7, 7.7 Hz, 3H), 7.39 (q, *J* = 8.3, 7.8 Hz, 3H), 7.33–7.23 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.36 (t, *J* = 3.6 Hz, 1H), 5.73 (dt, *J* = 6.0, 3.5 Hz, 1H), 5.46 (dt, *J* = 7.7, 3.6 Hz, 1H), 4.45 (dd, *J* = 11.5, 8.5 Hz, 1H), 3.99 (dd, *J* = 11.5, 4.0 Hz, 1H), 2.57 (ddd, *J* = 14.6, 5.7, 3.8 Hz, 1H), 2.49–2.34 (m, 3H), 1.65–1.50 (m, 2H), 1.50–1.37 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 164.8, 134.5, 133.4, 133.3, 131.9, 131.3, 130.3, 129.9, 129.6, 128.52, 128.46, 127.0, 125.1, 96.9, 91.1, 79.1, 67.4, 67.1, 60.5, 32.4, 30.7, 22.2, 19.7, 13.7; HRMS (MALDI) *m/z* calcd for $C_{32}H_{30}O_7Na$ $[M+Na]^+$ 549.1884, found 549.1890.

The α isomer: $[\alpha]_D^{22}$ = -154.2 (*c* 1.1, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.3 Hz, 2H), 7.99 (d, *J* = 7.4 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 2H), 7.63–7.54 (m, 4H), 7.49 (dt, *J* = 15.4, 7.5 Hz, 3H), 7.35 (t, *J* = 7.7 Hz, 3H), 6.69 (s, 1H), 5.82 (dt, *J* = 11.8,

4.6 Hz, 1H), 5.68 (s, 1H), 4.40 (d, *J* = 12.8 Hz, 1H), 4.16 (dd, *J* = 13.1, 2.4 Hz, 1H), 2.66 (td, *J* = 12.9, 3.4 Hz, 1H), 2.52 (q, *J* = 7.1 Hz, 2H), 2.35 (dd, *J* = 13.6, 4.2 Hz, 1H), 1.63 (m, 2H), 1.48 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.7, 165.4, 164.8, 134.8, 133.2, 133.1, 132.0, 130.8, 130.5, 129.74, 129.69, 129.54, 129.49, 128.4, 128.3, 127.2, 124.8, 96.5, 92.8, 79.6, 67.9, 66.3, 63.4, 30.7, 30.2, 22.0, 19.5, 13.6; HRMS (MALDI) *m/z* calcd for $C_{32}H_{30}O_7Na$ $[M+Na]^+$ 549.1884, found 549.1888.

**3,5-Di-*O*-benzyl-2-deoxy-D-ribofuranosyl *ortho*-hexynylbenzoate (1j)**



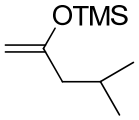

Compound **1j** was obtained (5.2 g, 84%; α/β = 1:1.2) as a colorless oil. A small portion of the anomers were separated. The α isomer: $[\alpha]_D^{29}$ = 43.3 (*c* 0.8, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.44–7.22 (m, 11H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 4.8 Hz, 1H), 4.66–4.38 (m, 5H), 4.27–4.12 (m, 1H), 3.66–3.51 (m, 2H), 2.48–2.34 (m, 4H), 1.71–1.55 (m, 2H), 1.52–1.42 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.4, 138.1, 134.4, 131.7, 130.8, 128.5, 127.8, 127.8, 127.1, 125.1, 99.6, 96.5, 85.0, 79.3, 78.9, 73.7, 71.5, 70.1, 38.4, 30.8, 22.2, 19.7, 13.8; HR-ESIMS *m/z* calcd for $C_{32}H_{34}O_5$ $[M+Na]^+$ 521.2299, found 521.2311.

The β isomer: $[\alpha]_D^{29}$ = 21.9 (*c* 1.3, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.38–7.12 (m, 11H), 6.62 (dd, *J* = 4.8, 0.8 Hz, 1H), 4.70–4.45 (m, 4H), 4.41–4.27 (m, 2H), 3.69–3.50 (m, 2H), 2.53 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.43–2.36 (m, 3H), 1.67–1.53 (m, 2H), 1.52–1.42 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.1, 138.0, 137.8, 134.4, 131.6, 131.4, 130.2, 128.4, 128.3, 127.8, 127.6, 127.0, 124.8, 99.4, 96.3, 84.2, 79.3, 79.0, 73.3, 71.7, 70.8, 39.0, 30.7, 22.0, 19.5, 13.6; HR-ESIMS *m/z* calcd for $C_{32}H_{34}O_5$ $[M+Na]^+$ 521.2299, found 521.2289.

**2.2. Typical procedure for the preparation of silyl enol ethers.** Silyl enol ethers were synthesized using a modified Corey's internal quench method. To a solution of *i*Pr$_2$NH (16.8 mL, 120 mmol) in THF (200 mL), BuLi (1.6 M solution in hexane, 66 mL, 106 mmol) was added dropwise in an ice bath, and the whole was stirred for 15 min. After cooling to –78 °C, a mixture of 4-methylpentan-2-one (12.5 mL, 100 mmol) and TMSCl (15 mL) in THF (40 mL) was added. After the addition was completed, the cooling bath was removed, and the mixture was stirred for 3 h at rt. Then, THF was evaporated and hexane was added. The resulting precipitate was filtrated off through a pad of celite, and the residue was washed with hexane. The combined filtrate was evaporated. The resulting residue was purified by distillation (bp. 115 $^{o}$C) to give **2d** (9.5g, 55%).

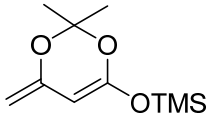
Silyl enol ether **2e** was synthesized using the same procedure. Silyl acetal **2f** was prepared through deprotonation by LDA in the presence of HMPA (25% v/v to THF) followed by the trap with TMSCl.

**4-Methyl-2-trimethylsilyloxy-1-pentene (2d)**



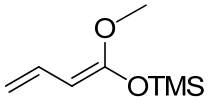

Compound **2d** was obtained (9.5 g, 55%) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 4.02 (d, $J$ = 14.9 Hz, 2H), 1.89-1.82 (m, 3H), 0.89 (d, $J$ = 6.4 Hz, 6H), 0.20 (s, 9H).

**(2,2-Dimethyl-6-methylene-6H-1,3-dioxin-4-yloxy)trimethylsilane (2e)**[S6]




Compound **2e** was obtained (5.6 g, 34%) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 4.62 (s, 1H), 4.04 (s, 1H), 3.85 (s, 1H), 1.52 (s, 6H), 0.24 (s, 9H).

**1-(Trimethylsiloxy)-1-methoxy-1,3-butadiene (2f)**[S7]




Compound **2f** was obtained (7.6 g, 54%) as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 6.49 (dt, *J* = 17.2, 10.4 Hz, 1H), 4.85 (ddd, *J* = 17.2, 2.1, 0.6 Hz, 1H), 4.60 (ddd, *J* = 10.5, 2.2, 0.7 Hz, 1H), 4.49 (d, *J* = 10.3 Hz, 1H), 3.58 (s, 3H), 0.23 (s, 9H).

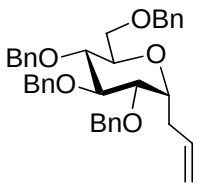
## 3. General Procedure for the *C*-Glycosylation

*Conditions A*: A mixture of **1b** (117 mg, 0.16 mmol), **2a** (0.038 mL, 0.20 mmol), and 4Å MS in dry $CH_2Cl_2$ (2 mL) under argon atmosphere was stirred at room temperature for 30 minutes. $Ph_3PAuNTf_2$ (14 mg, 0.02 mmol) was added, the stirring was continued at room temperature for 30 min. $Et_3N$ (0.1 mL) was added. The mixture was filtered through a pad of celite. The filtrates were concentrated in vaccum. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 4:1) to provide *C*-glycoside **3b** as a colorless syrup (77 mg, 85%, α only).

*Conditions B*: A mixture of **1b** (95 mg, 0.13 mmol), **2c** (17 mg, 0.087 mmol), and 5Å MS in dry toluene (2 mL) under argon atmosphere was stirred at room temperature for 30 minutes. $Ph_3PAuNTf_2$ (10 mg, 0.013 mmol) was added, the stirring was continued at room temperature for 30 min. $Et_3N$ (0.1 mL) was added. The mixture was filtered through a pad of celite, the filtrates were concentrated in vaccum. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 6:1) to provide *C*-glycoside **4a** as a colorless syrup (44 mg, 93%, α/β = 10:1).

## 4. Preparation and Characterization of the *C*-Glycosides

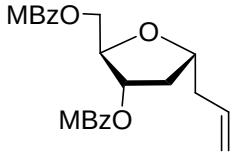
**Compound 3b**[S9]




*Conditions A* was applied to provide *C*-glycoside **3b** (77 mg, 85%, α only) as a

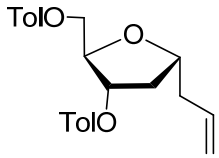
colorless oil.

**Compound 3c**



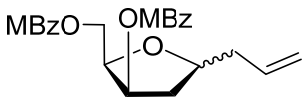

*Conditions A* was applied to provide *C*-glycoside **3c** (150 mg, 80%, α only) as a colorless oil: $[\alpha]_D^{23}$ = 44.0 (*c* 1.1, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (d, *J* = 1.6 Hz, 4 H), 6.93-6.88 (d, *J* = 8.8 Hz, 4 H), 5.84 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.51–5.43 (m, 1H), 5.17–5.06 (m, 2H), 4.55–4.29 (m, 4H), 3.85 (s, 3H), 3.84 (s, 3H), 2.66–2.48 (m, 2H), 2.40 (dt, *J* = 14.0, 6.9 Hz, 1H), 1.98 (ddd, *J* = 13.7, 5.9, 4.0 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.6, 165.4, 163.2, 163.1, 134.0, 131.31, 131.29, 121.9, 121.7, 117.1, 113.4, 113.3, 81.1, 78.1, 76.1, 64.2, 55.02, 49.97, 40.0, 36.6; HRMS (MALDI) *m/z* calcd for $C_{24}H_{26}O_7Na$ $[M+Na]^+$ 449.1566, found 449.1571.

**Compound 3d**



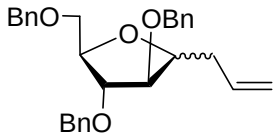

*Conditions A* was applied to provide *C*-glycoside **3d** (34 mg, 99%, α only) as a colorless oil: $[\alpha]_D^{22}$ = 34.3 (*c* 0.6, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 4H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 5.84 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.54–5.43 (m, 1H), 5.205.02 (m, 2H), 4.60–4.41 (m, 3H), 4.40–4.19 (m, 1H), 2.70–2.47 (m, 2H), 2.42–2.40 (m, 7H), 1.98 (ddd, *J* = 13.7, 5.9, 4.0 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 166.4, 166.2, 144.1, 143.8, 134.3, 129.72, 129.69, 129.2, 129.1, 127.1, 127.0, 117.5, 81.4, 78.6, 76.6, 64.7, 40.3, 37.1, 29.7, 21.7; LCMS (ESI-positive) *m/z* calcd for $C_{22}H_{26}O_3Na$ $[M+Na]^+$ 417.1673, found 417.1670.

**Compound 3e**



A mixture of **1e** (100 mg, 0.17 mmol), **2a** (0.032 ml, 0.20 mmol), and 4Å MS (300 mg) in dry $CH_2Cl_2$ (3 mL) under argon atmosphere was stirred at room temperature for 30 minutes. Then the mixture was stirred at -72 °C, $Ph_3PAuNTf_2$ (13 mg, 0.02 mmol) was added. The stirring was continued at -72 °C for one hour. $Et_3N$ (0.1 mL) was added. The mixture was filtered through a pad of celite. The filtrates were concentrated in vaccum. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 5:1) to provide *C*-glycoside **3e** as a colorless syrup (64 mg, 88%, α/β = 1:3). The β isomer: $[\alpha]_D^{24}$ = -41.0 (*c* 0.6, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 4H), 6.94–6.84 (m, 4H), 5.83 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.64 (ddd, *J* = 6.8, 4.6, 3.5 Hz, 1H), 5.08 (dd, *J* = 21.0, 5.4 Hz, 2H), 4.57 (qd, *J* = 11.6, 5.7 Hz, 2H), 4.30 (dd, *J* = 11.0, 5.0 Hz, 1H), 4.18–4.05 (m, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 2.55 (dq, *J* = 10.9, 6.8 Hz, 2H), 2.40 (dd, *J* = 14.0, 7.0 Hz, 1H), 1.88 (ddd, *J* = 14.0, 7.0, 3.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.1, 165.6, 163.6, 163.4, 134.1, 131.8, 131.7, 122.2, 117.5, 113.8, 113.6, 78.8, 77.6, 74.6, 63.1, 55.5, 55.4, 40.2, 38.1; HRMS (MALDI) *m/z* calcd for $C_{24}H_{26}O_7Na$ $[M+Na]^+$ 449.1559, found 449.1571.

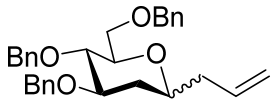
**Compound 3f**[S10]




*Conditions A* (with **1fβ** as donor) was applied to provide *C*-glycoside **3f** (77 mg, 87%, α/β = 1:2.5) as a colorless oil.

*Conditions A* (with **1fα** as donor) was applied to provide *C*-glycoside **3f** (58 mg, 80%, α/β = 1:2.5) as a colorless oil.

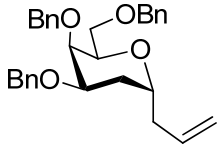
**Compound 3g**[S11]




*Conditions A* was applied to provide *C*-glycoside **3g** (98 mg, 80%, α/β = 13:1) as a

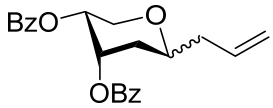
colorless oil.

**Compound 3h**



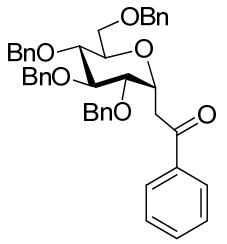

*Conditions A* was applied to provide *C*-glycoside **3h** (132 mg, 99%, α only) as a colorless oil: $[\alpha]_D^{23}$ = 24.8 (*c* 1.5, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 15H), 5.77 (ddt, *J* = 14.1, 10.6, 7.0 Hz, 1H), 5.14–4.93 (m, 1H), 4.80–4.40 (m, 6H), 4.14–3.95 (m, 2H), 3.94–3.84 (m, 1H), 3.85–3.73 (m, 2H), 3.69 (dd, *J* = 10.6, 4.3 Hz, 1H), 2.36 (dt, *J* = 13.8, 6.7 Hz, 1H), 2.17 (dt, *J* = 14.1, 7.1 Hz, 1H), 2.12–1.98 (m, 1H), 1.54 (ddd, *J* = 13.2, 6.5, 3.3 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 138.5, 134.8, 128.3, 128.24, 128.22, 127.7, 127.49, 127.45, 127.4, 127.2, 116.9, 74.9, 73.5, 73.3, 73.1, 72.4, 71.1, 67.7, 37.8, 31.9, 29.6; HRMS (MALDI) *m/z* calcd for $C_{30}H_{34}O_4Na$ $[M+Na]^+$ 481.2338, found 481.2349.

**Compound 3i**



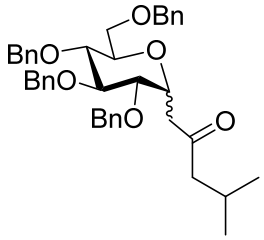

*Conditions A* was applied to provide *C*-glycoside **3i** (108 mg, 87%, α/β = 20:1) as a colorless oil. The α isomer: $[\alpha]_D^{22}$ = 88.3 (*c* 0.9, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.19–8.07 (m, 2H), 7.94–7.88 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 3H), 7.36 (t, *J* = 7.8 Hz, 2H), 5.98–5.77 (m, 2H), 5.31 (ddd, *J* = 10.7, 5.3, 3.0 Hz, 1H), 5.17 (dd, *J* = 19.9, 4.8 Hz, 2H), 4.13 (dd, *J* = 10.7, 5.3 Hz, 1H), 4.01 (t, *J* = 10.7 Hz, 1H), 3.97–3.87 (m, 1H), 2.36 (dtd, *J* = 20.2, 14.2, 6.4 Hz, 2H), 2.18 (ddd, *J* = 14.6, 3.7, 2.1 Hz, 1H), 1.99–1.83 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.5, 165.4, 134.0, 133.2, 133.1, 130.1, 129.62, 129.59, 129.5, 128.5, 128.3, 117.5, 71.7, 68.5, 68.0, 64.2, 39.6, 35.2; HRMS (MALDI) *m/z* calcd for $C_{22}H_{22}O_5Na$ $[M+Na]^+$ 389.1356, found 389.1359.

**Compound 4a**



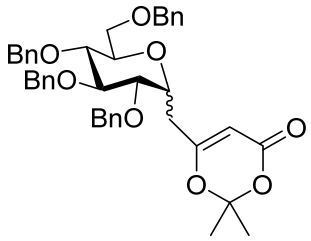

*Conditions B* was applied to provide *C*-glycoside **4a** (44 mg, 93%, α/β = 10:1) as a colorless oil. The α isomer: $[\alpha]_D^{26}$ = 38.0 (*c* 1.1, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.42–7.14 (m, 20H), 5.03–4.93 (m, 2H), 4.87 (dd, *J* = 10.8, 2.2 Hz, 2H), 4.69-4.48 (m, 5H), 3.87 (p, *J* = 9.1 Hz, 2H), 3.80–3.68 (m, 3H), 3.65 (d, *J* = 8.6 Hz, 1H), 3.50 (dd, *J* = 15.9, 5.2 Hz, 1H), 3.28 (dd, *J* = 15.9, 8.1 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 197.5, 138.6, 137.9, 133.0, 128.5, 128.4, 128.3, 128.2, 128.0, 127.90, 127.88, 127.81, 127.75, 127.6, 82.1, 79.4, 77.7, 75.3, 75.0, 73.4, 73.3, 72.5, 70.9, 68.8, 35.7; HRMS (MALDI) *m/z* calcd for $C_{42}H_{42}O_6Na$ $[M+Na]^+$ 665.2862, found 665.2874.

**Compound 4b**




*Conditions B* was applied to provide *C*-glycoside **4b** (81 mg, 77%, α/β = 10:1) as a colorless oil. The α isomer: $[\alpha]_D^{25}$ = 29.5 (*c* 1.3, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.51–6.89 (m, 20H), 4.95–4.75 (m, 3H), 4.71 (dt, *J* = 8.1, 5.6 Hz, 1H), 4.57-4.45 (m, 5H), 3.82–3.52 (m, 6H), 2.76 (dd, *J* = 15.6, 5.5 Hz, 1H), 2.69 (dd, *J* = 15.6, 8.2 Hz, 1H), 2.26 (d, *J* = 6.9 Hz, 2H), 2.08 (dp, *J* = 13.4, 6.7 Hz, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 207.9, 138.6, 138.2, 138.0, 128.5, 128.40, 128.36, 128.1, 128.0, 127.9, 127.8, 127.7, 82.2, 79.4, 77.8, 75.4, 75.0, 73.6, 73.4, 72.5, 70.7, 68.9, 52.5, 40.4, 24.3, 22.6, 22.5; HRMS (MALDI) *m/z* calcd for $C_{40}H_{46}O_6Na$ $[M+Na]^+$ 645.3170, found 645.3187.

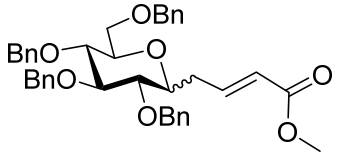
**Compound 4c**




*Conditions B* was applied to provide *C*-glycoside **4c** (111 mg, 65%, α/β = 1.2:1) as a colorless oil. A small portion of the anomers was separated. The α isomer: $[\alpha]_D^{25}$ = 63.4 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.39–7.00 (m, 20H), 5.26 (s, 1H), 4.67 (m, 8H), 4.31 (dd, *J* = 13.0, 7.4 Hz, 1H), 3.80–3.62 (m, 4H), 3.61–3.51 (m, 2H), 2.62 (d, *J* = 7.6 Hz, 2H), 1.65 (s, 3H), 1.62 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.9, 160.9, 138.3, 137.9, 137.8, 137.6, 128.5, 128.4, 128.4, 128.0, 127.94, 127.92, 127.87, 127.85, 127.8, 127.74, 127.71, 106.7, 95.2, 82.0, 79.2, 77.5, 75.5, 75.1, 73.54, 73.49, 71.7, 71.6, 68.4, 30.1, 25.8, 24.1; HRMS (ESI-positive) *m/z* calcd for $C_{41}H_{44}O_8Na$ $[M+Na]^+$ 687.2928, found 687.2930.

The β isomer: $[\alpha]_D^{25}$ = -18.7 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.55–7.13 (m, 20H), 5.38 (s, 1H), 4.96–4.54 (m, 8H), 3.84–3.62 (m, 4H), 3.56 (td, *J* = 9.5, 2.7 Hz, 1H), 3.43-3.34 (m, 2H), 2.76 (dd, *J* = 14.9, 2.3 Hz, 1H), 2.31 (dd, *J* = 14.9, 9.5 Hz, 1H), 1.69 (s, 3H), 1.63 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.7, 161.1, 138.3, 138.0, 137.8, 137.6, 128.52, 128.45, 128.39, 128.36, 128.1, 127.79, 127.76, 127.71, 127.68, 106.5, 95.5, 87.1, 81.1, 79.1, 78.3, 75.7, 75.6 75.2, 75.0, 73.4, 68.5, 36.0, 25.8, 24.0; HRMS (ESI-positive) *m/z* calcd for $C_{41}H_{44}O_8Na$ $[M+Na]^+$ 687.2928, found 687.2941.

**Compound 4d**

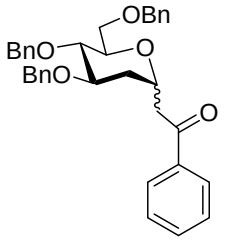



*Conditions B* was applied to provide *C*-glycoside **4d** (103 mg, 80%, α/β = 1.5:1) as a colorless oil. A small portion of the anomers was separated. The α isomer: $[\alpha]_D^{27}$ = -6.3 (*c* 0.5, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ7.47–7.09 (m, 20H), 7.04–6.90 (m,

1H), 5.93 (d, *J* = 15.7 Hz, 1H), 4.97–4.42 (m, 8H), 4.24–4.11 (m, 1H), 3.82–3.55 (m, 9H), 2.66–2.62 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.6, 145.4, 138.6, 138.1, 137.9, 128.5, 128.4, 128.3, 127.9, 127.88, 127.85, 127.8, 127.7, 127.6, 123.0, 79.7, 77.8, 75.4, 75.0, 73.5, 73.4, 73.2, 71.5, 68.7, 51.4, 28.5; HRMS (MALDI) *m/z* calcd for $C_{39}H_{42}O_7Na$ $[M+Na]^+$ 645.2823, found 645.2824.

The β isomer: $[\alpha]_D^{27}$ = 60.9 (*c* 1.3, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ7.39–7.14 (m, 20H), 7.07–6.97 (m, 1H), 5.88 (d, *J* = 15.7 Hz, 1H), 4.97–4.48 (m, 8H), 3.78–3.57 (m, 7H), 3.45–3.35 (m, 2H), 3.31 (t, *J* = 9.0 Hz, 1H), 2.68 (dd, *J* = 14.1, 6.4 Hz, 1H), 2.40 (dt, *J* = 15.0, 7.3 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.8, 145.4, 138.5, 138.2, 138.1, 137.9, 128.5, 128.45, 128.37, 128.3, 127.94, 127.90, 127.8, 127.73, 127.65, 127.6, 123.1, 87.2, 81.4, 79.1, 78.4, 77.7, 75.5, 75.1, 75.0, 73.5, 68.8, 51.4, 34.4; HRMS (MALDI) *m/z* calcd for $C_{39}H_{42}O_7Na$ $[M+Na]^+$ 645.2823, found 645.2821.

**Compound 4e**

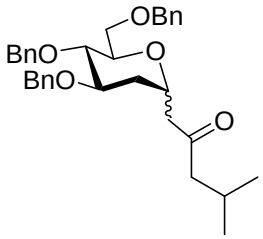



*Conditions A* was applied to provide *C*-glycoside **4e** (32 mg, 82%, α/β = 5.4:1) as a colorless oil. A small portion of the anomers was separated. The α isomer: $[\alpha]_D^{26}$ = 13.9 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.45–7.16 (m, 15H), 4.79 (d, *J* = 11.3 Hz, 1H), 4.76–4.68 (m, 1H), 4.68–4.50 (m, 5H), 3.94 (dd, *J* = 10.0, 5.5 Hz, 1H), 3.86 (m, 2H), 3.75 (dd, *J* = 10.3, 3.8 Hz, 1H), 3.60 (t, *J* = 6.5 Hz, 1H), 3.42 (dd, *J* = 16.0, 5.9 Hz, 1H), 3.16 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.20–2.06 (m, 1H), 2.03–1.90 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 197.8, 138.3, 137.0, 133.2, 128.6, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 75.8, 75.7, 74.0, 73.6, 73.4, 71.1, 69.0, 66.9, 41.9, 32.5; HRMS (MALDI) *m/z* calcd for $C_{35}H_{36}O_5Na$ $[M+Na]^+$ 559.2435, found 559.2455.

The β isomer: $^1$H NMR (400 MHz, $CDCl_3$) δ 8.02–7.90 (m, 2H), 7.63–7.53 (m, 1H),

7.53–7.42 (m, 2H), 7.41–7.05 (m, 15H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.83–4.39 (m, 5H), 4.06 (dddd, *J* = 11.4, 7.3, 5.5, 1.9 Hz, 1H), 3.88–3.66 (m, 3H), 3.62–3.37 (m, 3H), 3.07 (dd, *J* = 16.8, 7.0 Hz, 1H), 2.40 (ddd, *J* = 12.6, 5.0, 1.9 Hz, 1H), 1.47 (dt, *J* = 12.7, 11.3 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 197.9, 138.66, 138.65 138.4 137.2 133.4, 128.8, 128.53, 128.45, 128.4, 128.3, 128.1, 127.9, 127.8, 127.72, 127.66, 81.05, 79.1, 78.4, 75.1, 73.6, 72.2, 71.6, 69.5, 44.6, 37.0.

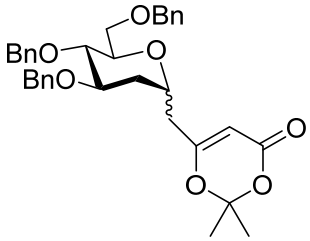
**Compound 4f**




*Conditions A* was applied to provide *C*-glycoside **4f** (52 mg, 74%, α/β = 2:1) as a colorless oil. A small portion of the anomers was separated. The α isomer: $[\alpha]_D^{27}$ = 25.2 (*c* 1.3, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42–7.13 (m, 15H), 4.79–4.39 (m, 7H), 3.88–3.61 (m, 4H), 3.52 (t, *J* = 6.5 Hz, 1H), 2.78 (dd, *J* = 15.6, 7.4 Hz, 1H), 2.46 (dd, *J* = 15.7, 6.5 Hz, 1H), 2.30 (d, *J* = 6.9 Hz, 2H), 2.21–2.04 (m, 1H), 2.00–1.89 (m, 1H), 1.88–1.76 (m, 1H), 0.89 (d, *J* = 2.1 Hz, 3H), 0.88 (d, *J* = 2.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 208.6, 138.2, 128.40, 128.36, 128.3, 128.0, 127.8, 127.7, 127.63, 127.58, 75.8, 75.6, 73.7, 73.4, 71.2, 68.9, 66.7, 52.6, 46.3, 32.7, 24.4, 22.6; HRMS (MALDI) *m/z* calcd for $C_{33}H_{40}O_5Na$ $[M+Na]^+$ 539.2768, found 539.2755.

The β isomer: $[\alpha]_D^{27}$ = 27.6 (*c* 0.8, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53–6.98 (m, 15H), 4.98–4.41 (m, 6H), 3.90–3.78 (m, 1H), 3.75–3.61 (m, 3H), 3.50 (t, *J* = 9.1 Hz, 1H), 3.38 (m, 1H), 2.82 (dd, *J* = 16.3, 6.5 Hz, 1H), 2.45 (dd, *J* = 16.3, 6.0 Hz, 1H), 2.37–2.26 (m, 2H), 2.26–2.19 (m, 1H), 2.13 (tt, *J* = 13.4, 6.7 Hz, 1H), 1.38 (dd, *J* = 23.7, 11.5 Hz, 1H), 0.91 (d, *J* = 0.7 Hz, 3H), 0.89 (d, *J* = 0.7 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 208.6, 138.5, 138.4, 128.2, 128.3, 127.9, 127.8, 127.6, 127.54, 127.47, 80.8, 78.8, 78.1, 74.9, 73.4, 71.7, 71.4, 69.2, 52.8, 48.6, 36.7, 24.3, 22.5, 22.4; HRMS (MALDI) *m/z* calcd for $C_{33}H_{40}O_5Na$ $[M+Na]^+$ 539.2768, found 539.2767.

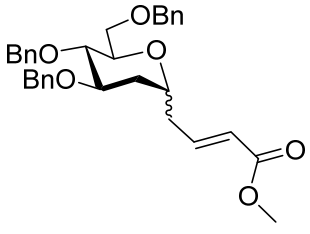
**Compound 4g**




*Conditions A* was applied to provide *C*-glycoside **4g** (111 mg, 90%, α/β = 1:1.3) as a colorless oil. A small portion of the anomers was separated. The α isomer: $[\alpha]_D^{25}$ = 52.2 (*c* 0.7, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.41–7.22 (m, 15H), 5.32 (s, 1H), 4.82–4.47 (m, 6H), 4.33 (dq, *J* = 9.8, 5.0 Hz, 1H), 3.85–3.75 (m, 3H), 3.71–3.64 (m, 1H), 3.61 (t, *J* = 6.5 Hz, 1H), 2.65 (dd, *J* = 14.7, 9.3 Hz, 1H), 2.32 (dd, *J* = 14.7, 5.1 Hz, 1H), 1.98 (dt, *J* = 13.5, 4.7 Hz, 1H), 1.86 (ddd, *J* = 13.4, 8.5, 4.7 Hz, 1H), 1.68 (s, 3H), 1.68 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.3, 161.0, 138.08, 138.05, 137.9, 128.5, 128.4, 128.3, 127.9, 127.81, 127.79, 127.76, 127.7, 127.6, 106.6, 95.1, 75.6, 73.8, 73.4, 73.2, 71.5, 68.5, 67.3, 37.0, 32.8, 25.4, 24.6; HRMS (ESI-positive) *m/z* calcd for $C_{34}H_{38}O_7Na$ $[M+Na]^+$ 581.2510, found 581.2513.

The β isomer: $[\alpha]_D^{25}$ = 6.5 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 15H), 5.34 (s, 1H), 4.96–4.43 (m, 6H), 3.72–3.56 (m, 4H), 3.51 (t, *J* = 9.1 Hz, 1H), 3.34 (d, *J* = 9.5 Hz, 1H), 2.52 (dd, *J* = 14.7, 8.3 Hz, 1H), 2.36 (dd, *J* = 14.7, 4.2 Hz, 1H), 2.11 (dd, *J* = 12.4, 3.9 Hz, 1H), 1.64 (s, 3H), 1.60 (s, 3H), 1.47 (dd, *J* = 23.8, 11.7 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 168.2, 161.0, 138.32, 138.31, 138.0, 128.4, 128.32, 128.31, 127.9, 127.71, 127.67, 127.61, 127.59, 106.5, 95.3, 80.6, 79.1, 78.0, 75.0, 73.4, 72.0, 71.6, 69.0, 39.7, 36.7, 25.6, 24.3; HRMS (ESI-positive) *m/z* calcd for $C_{34}H_{38}O_7Na$ $[M+Na]^+$ 581.2510, found 581.2528.

**Compound 4h**

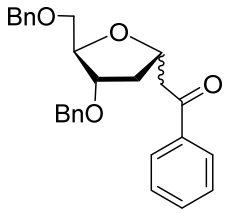



*Conditions A* was applied to provide *C*-glycoside **4h** (70 mg, 70%, α/β = 1.3:1) as a

colorless oil. A small portion of the anomers was separated. The α isomer: $[\alpha]_D^{27}$ = 9.7 (*c* 1.0, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.47–7.18 (m, 15H), 7.09–6.99 (m, 1H), 5.96 (d, *J* = 15.7 Hz, 1H), 4.99–4.55 (m, 6H), 3.83–3.64 (m, 6H), 3.60–3.49 (m, 2H), 3.45 (ddd, *J* = 9.6, 4.3, 2.0 Hz, 1H), 2.60 (ddd, *J* = 14.8, 6.8, 1.3 Hz, 1H), 2.45 (dt, *J* = 7.7, 6.6 Hz, 1H), 2.24–2.14 (m, 1H), 1.49 (dd, *J* = 24.0, 11.5 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 166.7, 144.8, 138.5, 138.4, 138.3, 128.4, 128.3, 127.9, 127.7, 127.6, 127.5, 123.2, 80.8, 79.1, 78.3, 75.0, 74.0, 73.4, 71.4, 69.3, 51.4, 38.2, 36.5; HRMS (MALDI) *m/z* calcd for $C_{32}H_{36}O_6Na$ $[M+Na]^+$ 539.2404, found 539.2409.

The β isomer: $[\alpha]_D^{27}$ = 32.4 (*c* 1.2, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.40–7.18 (m, 15H), 6.99–6.88 (m, 1H), 5.89 (d, *J* = 15.7 Hz, 1H), 4.80–4.49 (m, 6H), 4.16–4.07 (m, 1H), 3.87–3.75 (m, 3H), 3.75–3.64 (m, 4H), 3.56 (t, *J* = 6.6 Hz, 1H), 2.60 (ddd, *J* = 15.0, 8.2, 1.3 Hz, 1H), 2.43–2.22 (m, 1H), 1.96 (dt, *J* = 13.4, 4.7 Hz, 1H), 1.79 (ddd, *J* = 13.3, 8.5, 4.6 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 166.6, 144.9, 138.24, 138.17, 138.1, 128.4, 128.30, 128.25, 127.9, 127.7, 127.6, 127.54, 127.50, 123.0, 75.8, 75.7, 73.7, 73.3, 73.1, 71.3, 69.0, 68.7, 51.4, 35.5, 32.5; HRMS (MALDI) *m/z* calcd for $C_{32}H_{36}O_6Na$ $[M+Na]^+$ 539.2404, found 539.2408.

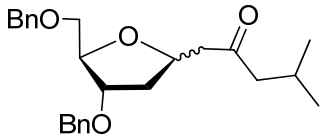
**Compound 4i**




*Conditions A* was applied to provide *C*-glycoside **4i** (88 mg, 96%, α/β = 6.2:1) as a colorless oil. The α isomer: $[\alpha]_D^{24}$ = 41.9 (*c* 0.8, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.39–7.16 (m, 10H), 4.78–4.68 (m, 1H), 4.52 (m, 4H), 4.27 (dd, *J* = 8.1, 4.9 Hz, 1H), 4.11 (dt, *J* = 6.6, 3.4 Hz, 1H), 3.60–3.39 (m, 3H), 3.26 (dd, *J* = 16.6, 7.7 Hz, 1H), 2.46 (dt, *J* = 13.5, 6.9 Hz, 1H), 1.98–1.76 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 198.6, 138.1, 138.0, 137.0, 133.1, 128.5, 128.4, 128.3, 128.2, 127.6, 82.5, 81.0, 75.5, 73.4, 71.4, 70.8, 44.9, 37.6; HRMS (MALDI) *m/z* calcd for $C_{27}H_{28}O_4Na$ $[M+Na]^+$ 439.1867,

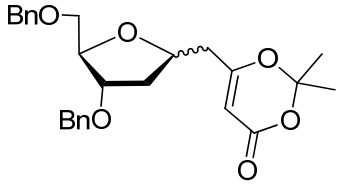
found 439.1880.

**Compound 4j**




*Conditions A* was applied to provide *C*-glycoside **4j** (75 mg, 90%, α/β = 3.5:1) as a colorless oil. The α/β anomers were inseparable. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.35–7.24 (m, 10 H), 4.62–4.52 (m, 2.8H), 4.51–4.44 (m, 2.2H), 4.19 (td, *J* = 5.0, 3.3 Hz, 0.8H), 4.11–4.05 (m, 1H), 4.04–4.00 (m, 0.2H), 3.56–3.36 (m, 2H), 2.91 (dd, *J* = 16.5, 6.4 Hz, 0.8H), 2.78 (dd, *J* = 16.0, 6.4 Hz, 0.2H), 2.64 (dd, *J* = 16.5, 7.0 Hz, 0.8H), 2.52 (dd, *J* = 16.1, 6.1 Hz, 0.2H), 2.37 (dt, *J* = 13.5, 6.9 Hz, 1H), 2.31–2.26 (m, 2H), 2.25–2.19 (m, 0.2H), 2.17–2.06 (m, 1H), 1.78–1.70 (m, 1H), 1.60 (ddd, *J* = 13.1, 10.1, 6.3 Hz, 0.2H), 0.90 (d, *J* = 6.6 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) the major α: δ 209.4, 138.1, 138.0, 128.3, 127.6, 82.4, 82.3, 80.9, 74.84, 74.81, 73.3, 71.4, 70.7, 52.6, 49.3, 37.7, 24.4, 22.5; the minor β: δ 208.6, 138.1, 138.0, 128.5, 128.4, 128.1, 127.7, 127.4, 81.9, 81.0, 80.8, 74.97, 74.96, 73.4, 73.3, 71.4, 71.3, 70.7, 70.6, 52.5, 49.2, 48.7, 37.7; HRMS (MALDI) *m/z* calcd for $C_{25}H_{32}O_4Na$ $[M+Na]^+$ 419.2199, found 419.2193.

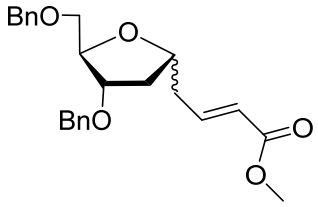
**Compound 4k**




*Conditions A* was applied to provide *C*-glycoside **4k** (134 mg, 83%, α/β = 1.5:1) as a colorless oil. The α/β anomers were inseparable. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.36–7.26 (m, 10H), 5.31 (s, 1H), 4.50–4.53 (m, 4.4H), 4.39–4.34 (m, 1.2H), 4.22–4.20 (m, 0.7H), 4.12 (dt, *J* = 6.1, 3.1 Hz, 1.1H), 4.07–4.05 (m, 0.4H), 3.53–3.44 (m, 2.2H), 2.67 (dd, *J* = 14.5, 7.7 Hz, 0.7H), 2.54–2.37 (m, 1.5H), 2.29 (dt, *J* = 13.5, 6.9 Hz, 0.7H), 2.15–2.04 (m, 0.4H), 1.87–1.79 (m, 0.7H), 1.72-1.65 (m, 7.25H) ; $^{13}$C

NMR (100 MHz, $CDCl_3$) δ 168.9, 168.6, 161.14, 161.12, 138.0, 137.94, 137.91, 128.43, 128.42, 128.3 127.7, 127.63, 127.58, 127.52, 127.49, 106.5, 106.4, 94.9 94.8, 83.8, 82.8, 80.9, 80.7, 75.5, 75.0, 73.44, 73.39, 71.5, 71.1, 70.8, 70.7, 40.2, 39.6, 38.2, 37.4, 25.23, 25.20, 24.8, 24.7; HRMS (ESI-positive) *m/z* calcd for $C_{26}H_{30}O_6Na$ $[M+Na]^+$ 461.1935, found 461.1952.

**Compound 4l**




*Conditions A* was applied to provide *C*-glycoside **4l** (95 mg, 80%, α/β = 1.7:1) as a colorless oil. A small portion of the anomers was separated. The α isomer: $[\alpha]_D^{27}$ = 32.2 (*c* 0.7, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.42–7.17 (m, 10H), 7.01–6.87 (m, 1H), 5.89 (d, *J* = 15.7 Hz, 1H), 4.61–4.42 (m, 4H), 4.26–4.14 (m, 2H), 4.10 (dt, *J* = 8.2, 4.3 Hz, 1H), 3.72 (s, 3H), 3.50 (dd, *J* = 4.6, 2.0 Hz, 2H), 2.63 (dt, *J* = 13.7, 6.9 Hz, 1H), 2.47 (dt, *J* = 14.5, 7.2 Hz, 1H), 2.29 (dt, *J* = 13.3, 6.8 Hz, 1H), 1.82–1.73 (m, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 166.8, 145.4, 138.1, 138.0, 128.39, 128.35, 127.7, 127.60, 127.59, 123.0, 82.5, 80.7, 77.3, 73.4, 71.6, 70.7, 51.4, 38.8, 37.4; HRMS (ESI-positive) *m/z* calcd for $C_{24}H_{28}O_5Na$ $[M+Na]^+$ 419.1829, found 419.1824.

The β isomer: $[\alpha]_D^{27}$ = 21.8 (*c* 0.3, $CHCl_3$); $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.44–7.19 (m, 10H), 7.05–6.90 (m, 1H), 5.90 (d, *J* = 15.7 Hz, 1H), 4.62–4.44 (m, 4H), 4.30–4.19 (m, 1H), 4.13 (dt, *J* = 7.5, 3.9 Hz, 1H), 4.02 (d, *J* = 6.4 Hz, 1H), 3.72 (s, 3H), 3.54 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.45 (dd, *J* = 10.2, 5.3 Hz, 1H), 2.59–2.48 (m, 1H), 2.48–2.39 (m, 1H), 2.12–2.04 (m, 1H), 1.65 (ddd, *J* = 13.1, 10.3, 6.3 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 166.7, 145.0, 138.2, 138.0, 128.39, 128.35, 127.64, 127.63, 127.59, 127.57, 123.1, 83.6, 81.0, 77.1, 73.4, 71.05, 70.91, 51.4, 37.8, 37.8; HRMS (ESI-positive) *m/z* calcd for $C_{24}H_{28}O_5Na$ $[M+Na]^+$ 419.1829, found 419.1824.

## 5. Mechanistic Studies

**5.1. NMR studies on the stability of allyltrimethylsilane (2a) in the presence of $Ph_3PAuOTf$ and $Ph_3PAuNTf_2$.**

To a NMR tube was added the gold complex and $CDCl_3$, followed by the addition of an appropriate amount of allyltrimethylsilane (**2a**). Then the tube was shaken vigorously and subjected immediately to NMR analysis at room temperature (Figure S1). The $^1H$ NMR signals of allyltrimethylsilane were largely remained within 30 min in the presence of $Ph_3PAuNTf_2$. However, in the case of $Ph_3PAuOTf$, new peaks at ~5.0 and 1.7 ppm appeared quickly, which is assignable to propene.

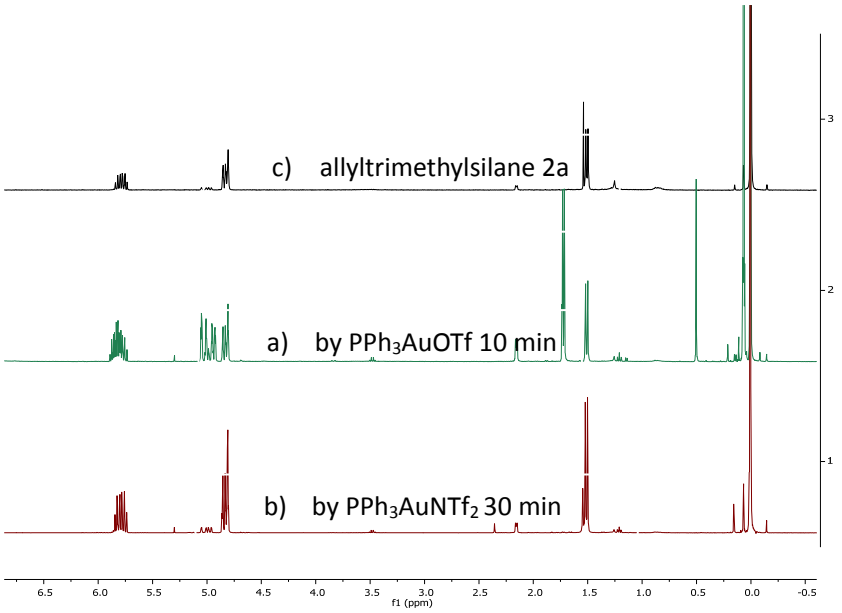
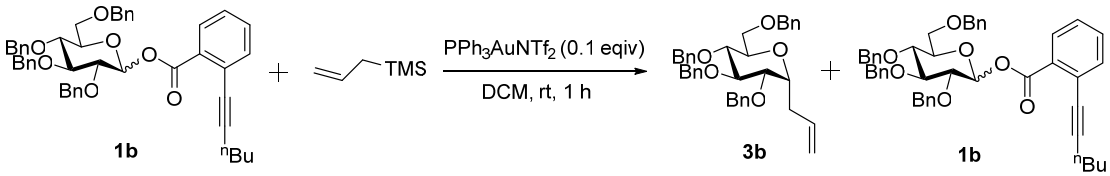



**Figure S1**. $^1H$ NMR analysis of allyltrimethylsilane **2a** in the presence of $Ph_3PAuNTf_2$ or $Ph_3PAuOTf$ in $CDCl_3$ at RT.

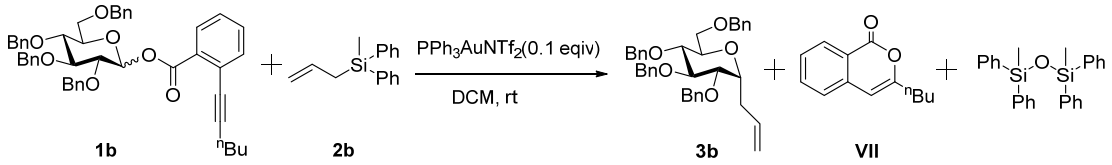
**5.2. *C*-Glycosylation under anhydrous conditions in the absence of molecular sieves.**




A 25 mL glass Schlenk flask fitted with a re-sealable Teflon valve was equipped with a magnetic stir bar and charged with glycosyl *ortho*-alkynylbenzoate **1b** (300 mg,

0.41 mmol). The flask was heated at 100 ºC for 10 min under high vacuum, then allowed to cool to room temperature and filled with argon. 4Å MS (300 mg), 6 mL dry $CH_2Cl_2$, and allyltrimethylsilane **2a** (98 μL, 0.61 mmol) were added under argon atmosphere. The valve was closed and the suspension stirred at room temperature for 30 min. The supernatant was taken via a syringe into a dry flask containing a dry $CH_2Cl_2$ solution of $PPh_3AuNTf_2$ (31 mg, 0.1 equiv). 30 min later, $Et_3N$ (0.15 mL) was added into the flask, and stirred for 5 min. The mixture was filtered through a pad of celite, the filtrates were concentrated in vaccum. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 10:1) to provide *C*-glycoside **3b** (30 mg, 13%) as a colorless syrup and to recover glycosyl *ortho*-alkynylbenzoate **1b** (222 mg, 74%).

### 5.3. Isolation and charaterization of $(Ph_2MeSi)_2O$ from the *C*-glycosylation of glucopyranosyl *ortho*-henxynylbenzoate (1b) with allyldiphenylmethylsilane (2b).




A mixture of **1b** (522 mg, 0.72 mmol), **2b** (205 mg, 0.86 mmol), and 4Å MS in dry $CH_2Cl_2$ (10 mL) under argon atmosphere was stirred at room temperature for 30 minutes. $Ph_3PAuNTf_2$ (53 mg, 0.072 mmol) was added, and the stirring was continued at room temperature for one hour. $Et_3N$ (0.5 mL) was added. The mixture was filtered through a pad of celite, the filtrates were concentrated in vaccum. The residue was purified by silica gel column chromatography (hexane-ethyl acetate, 7:1) to provide *C*-glycoside **3b** as a colorless syrup (369 mg, 91%), isocoumarin **VII** (142 mg, 98%) as a light yellow solid, and $(Ph_2MeSi)_2O$[S8] (165 mg, 93%).

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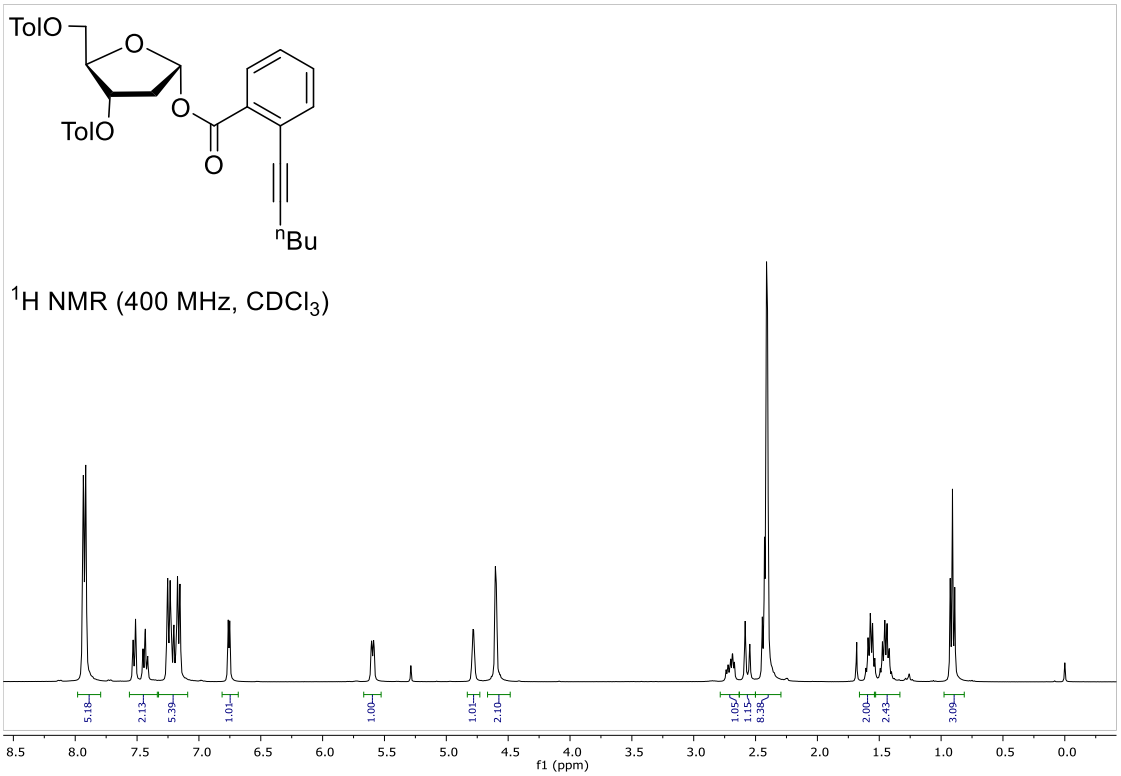
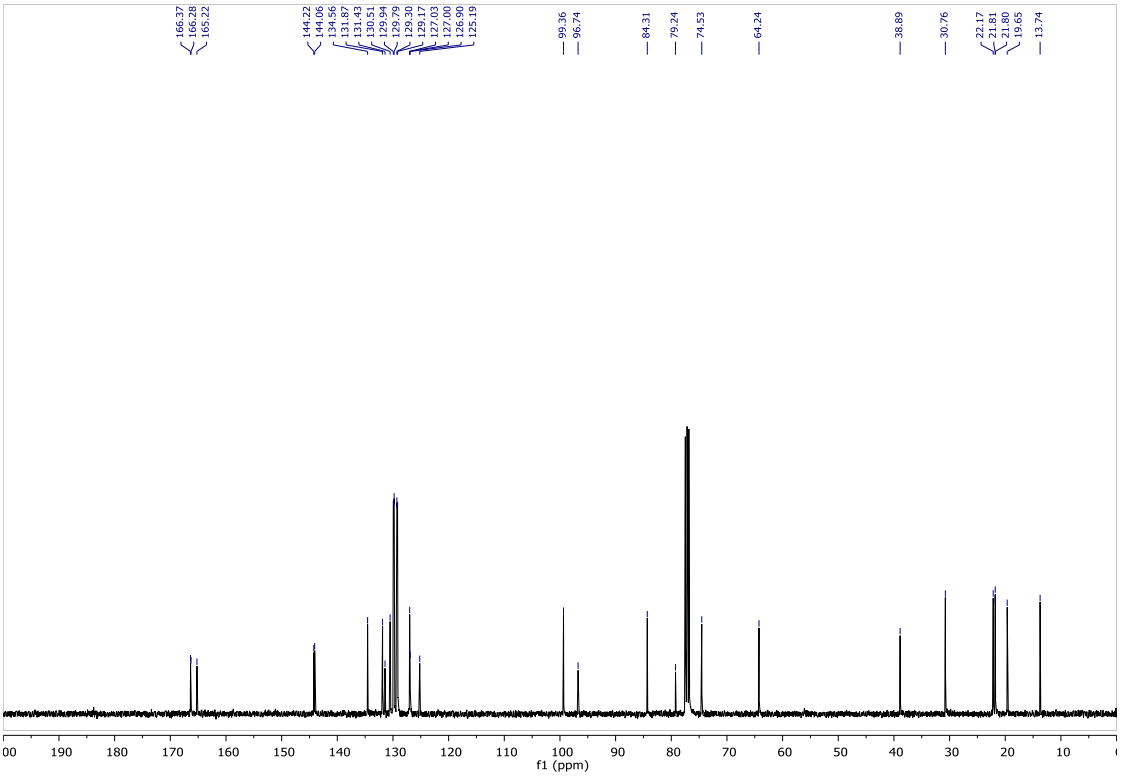
## 3,5-Di-*O*-toluoyl-2-deoxy-α-D-ribofuranosyl *ortho*-hexynylbenzoate (1dα)




$^{13}$C NMR (100 MHz, $CDCl_3$)



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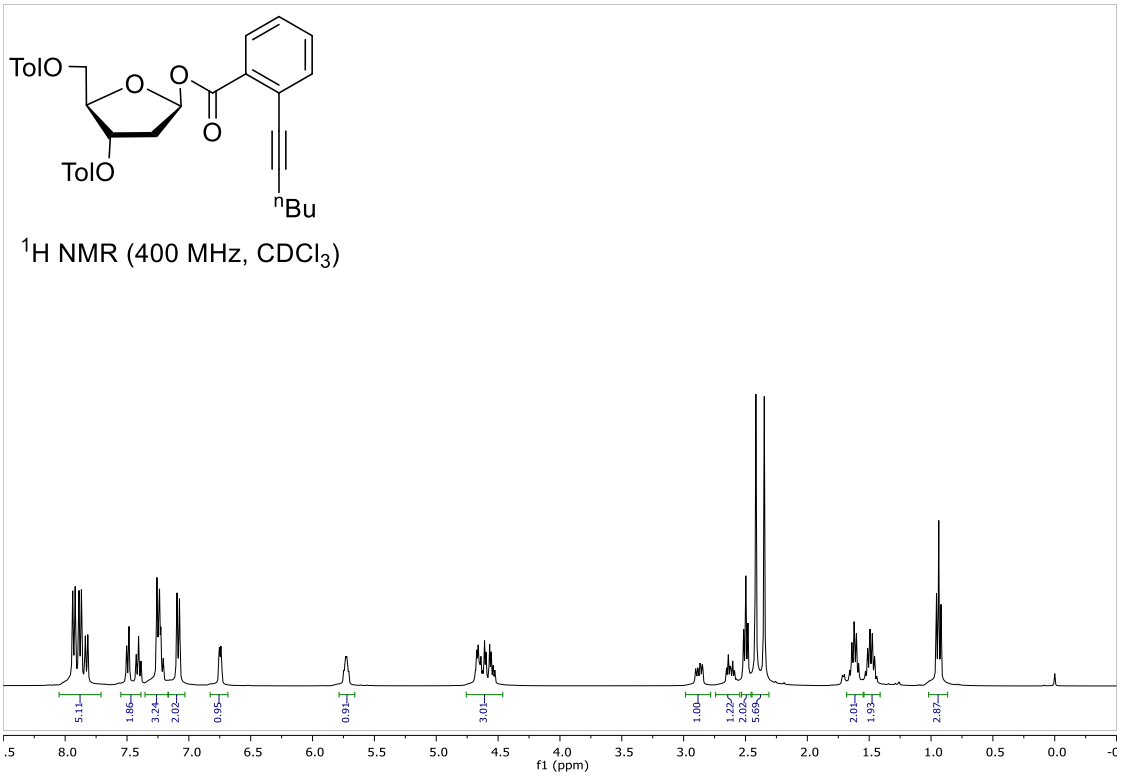


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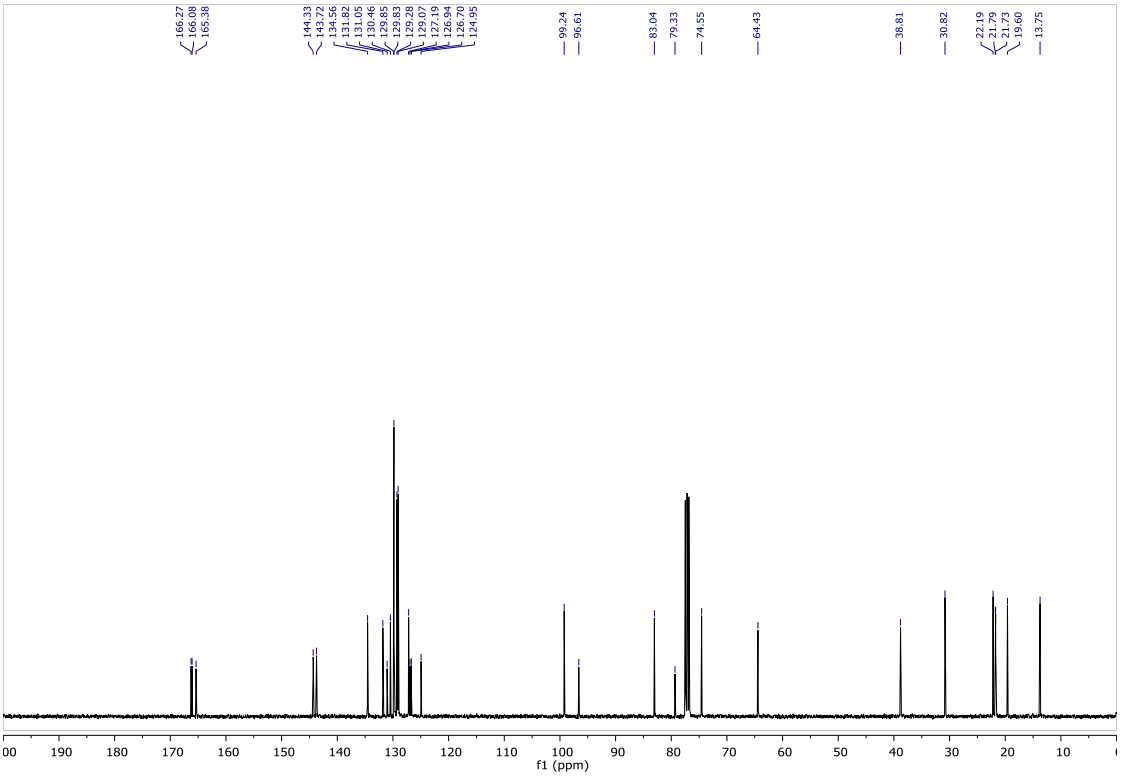
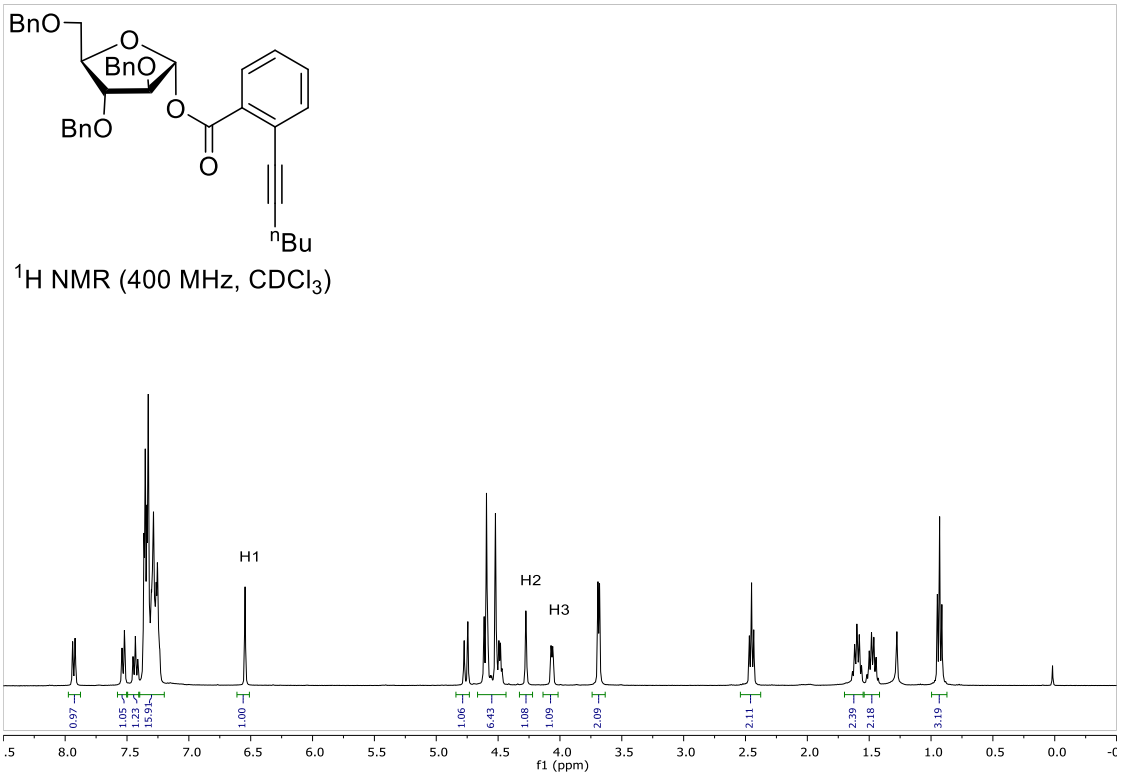


## 2,3,5-Tri-*O*-benzyl-α-D-arabinofuranosyl *ortho*-hexynylbenzoate (1fα)

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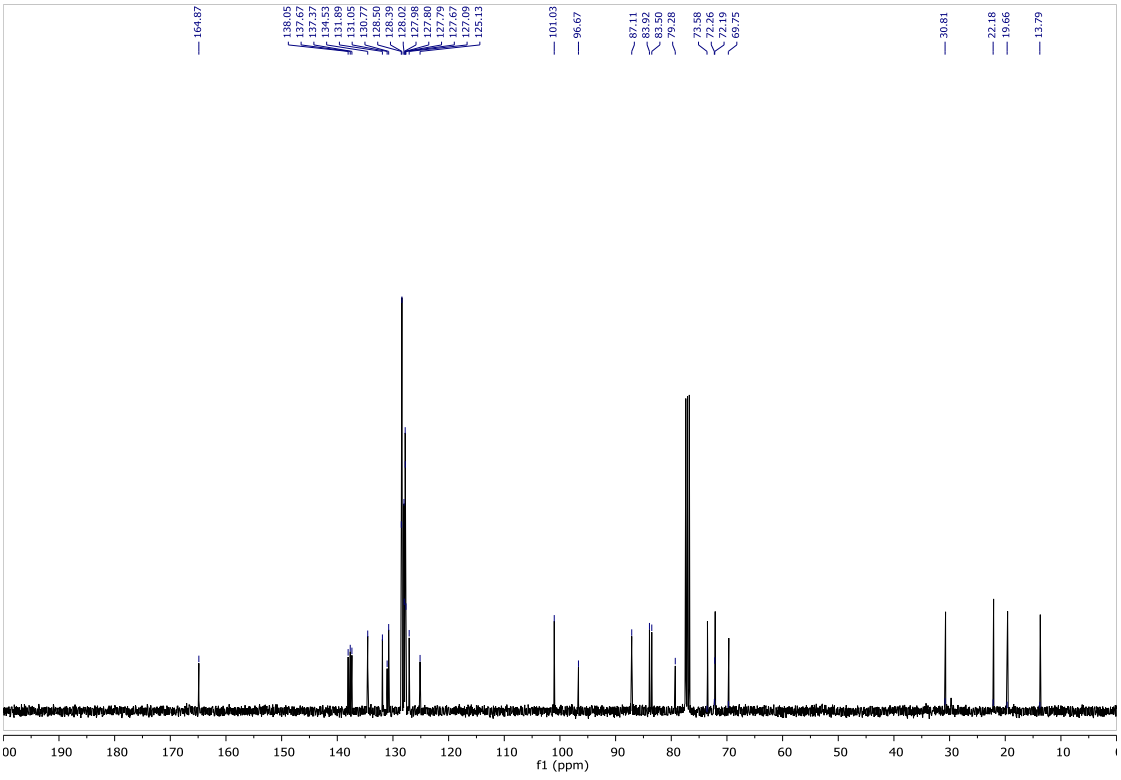

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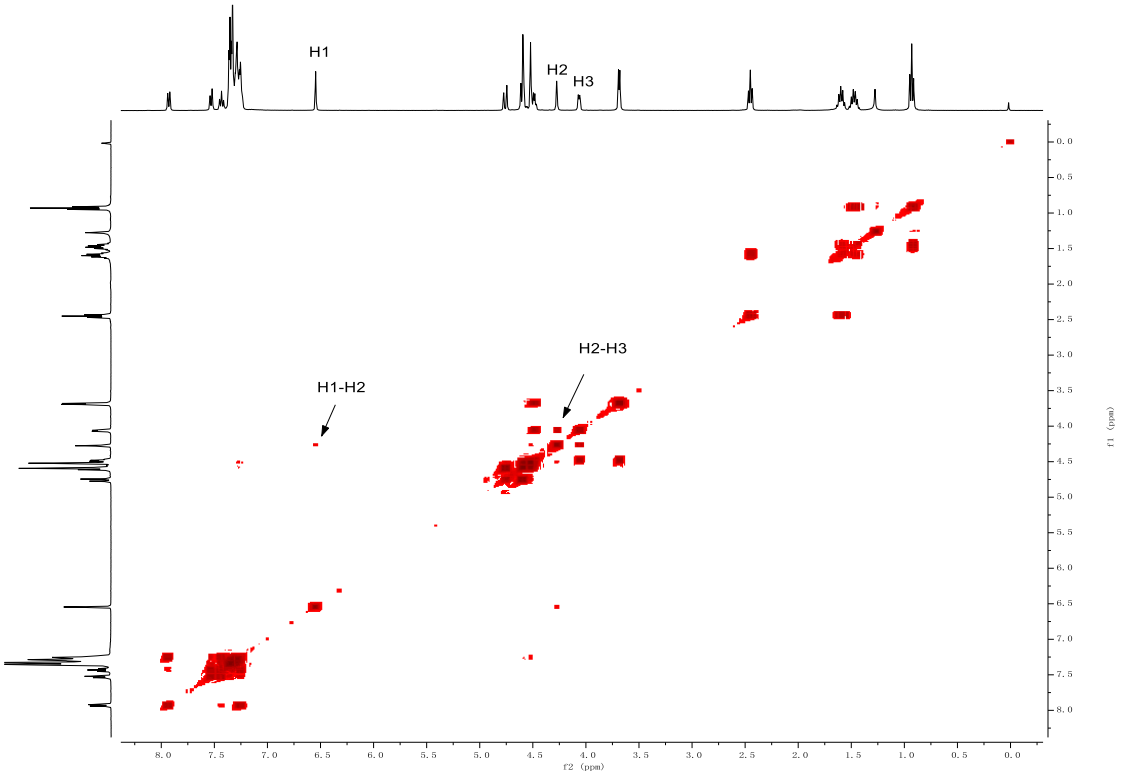


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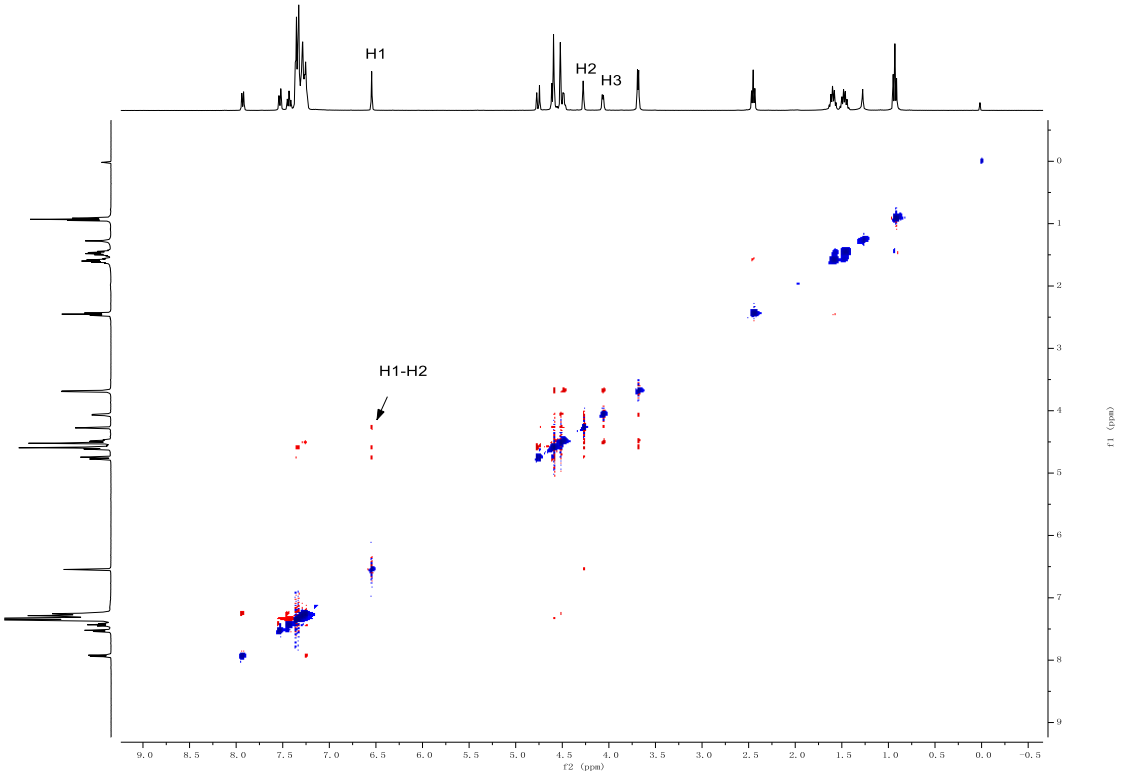

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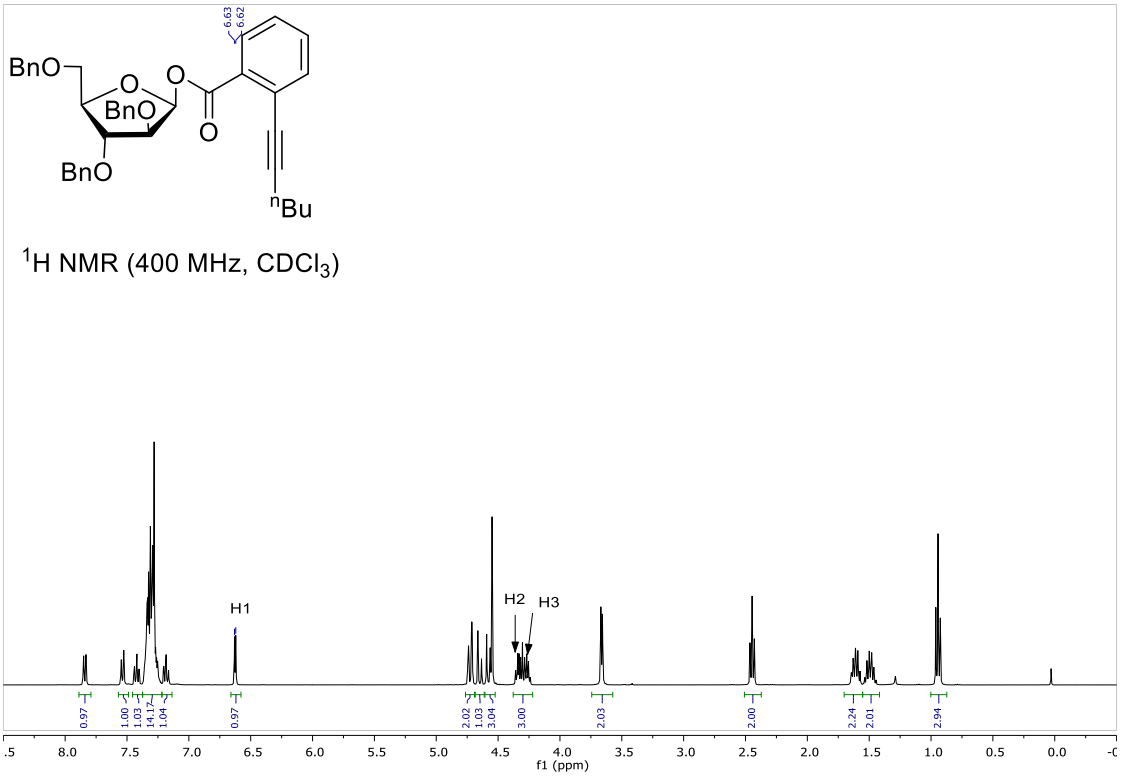


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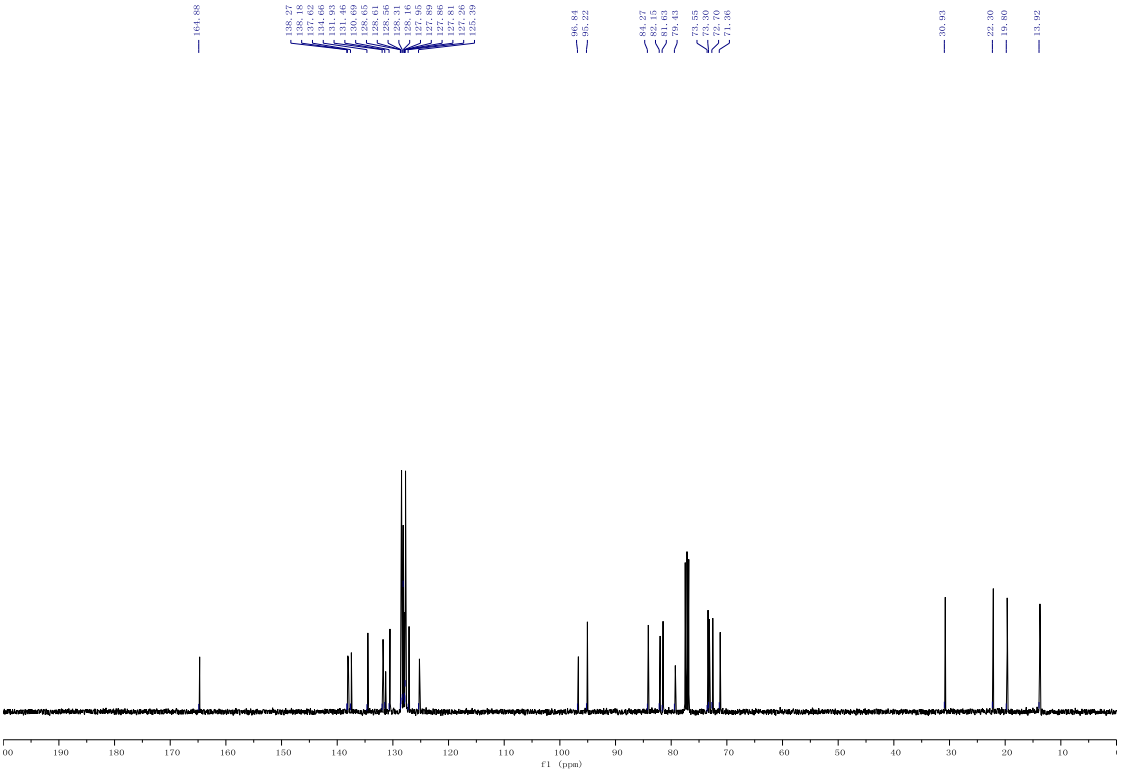

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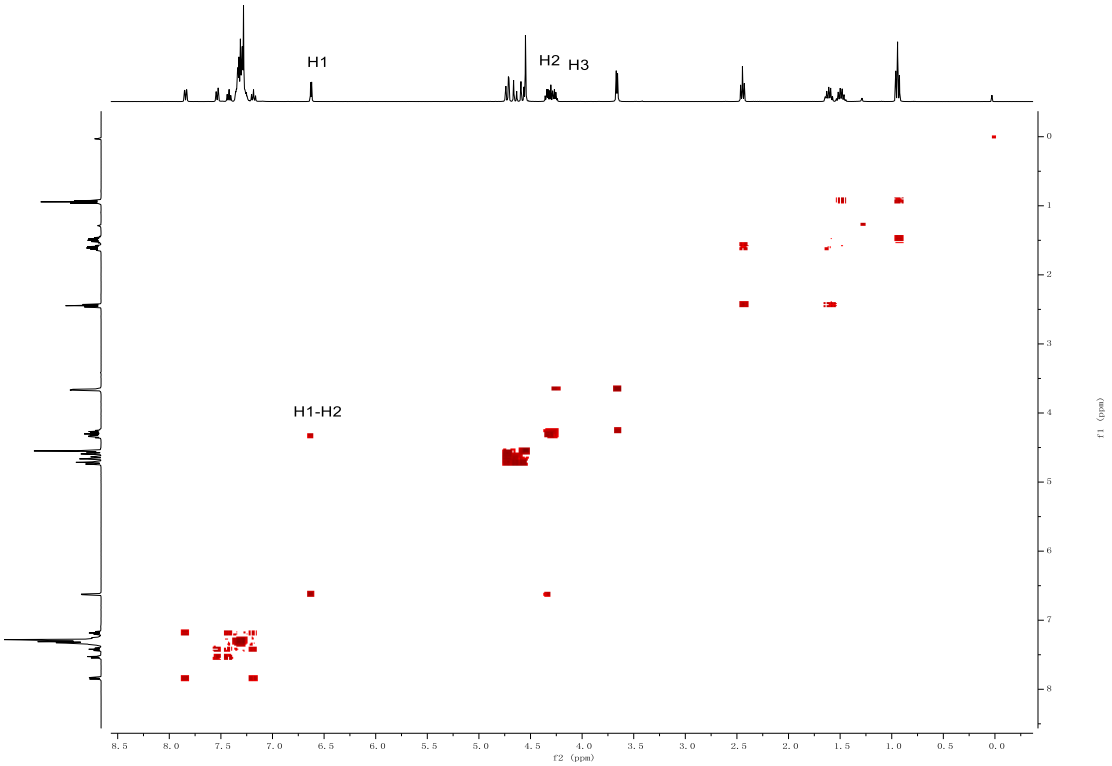


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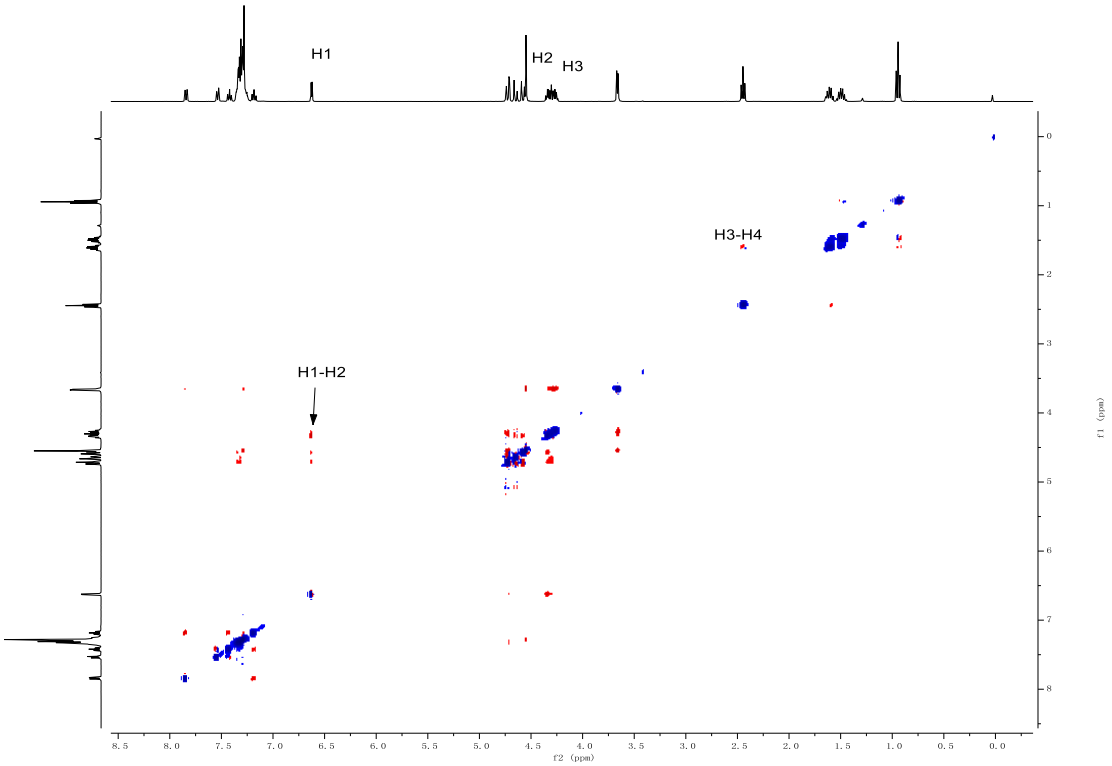

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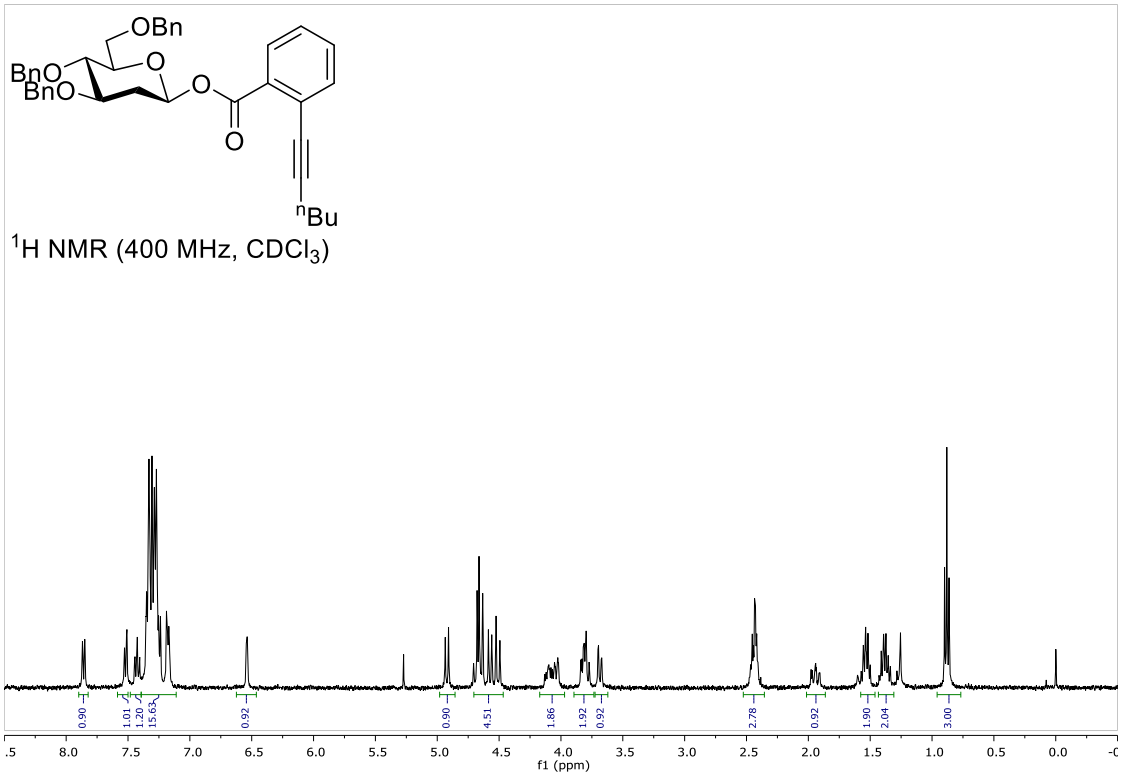


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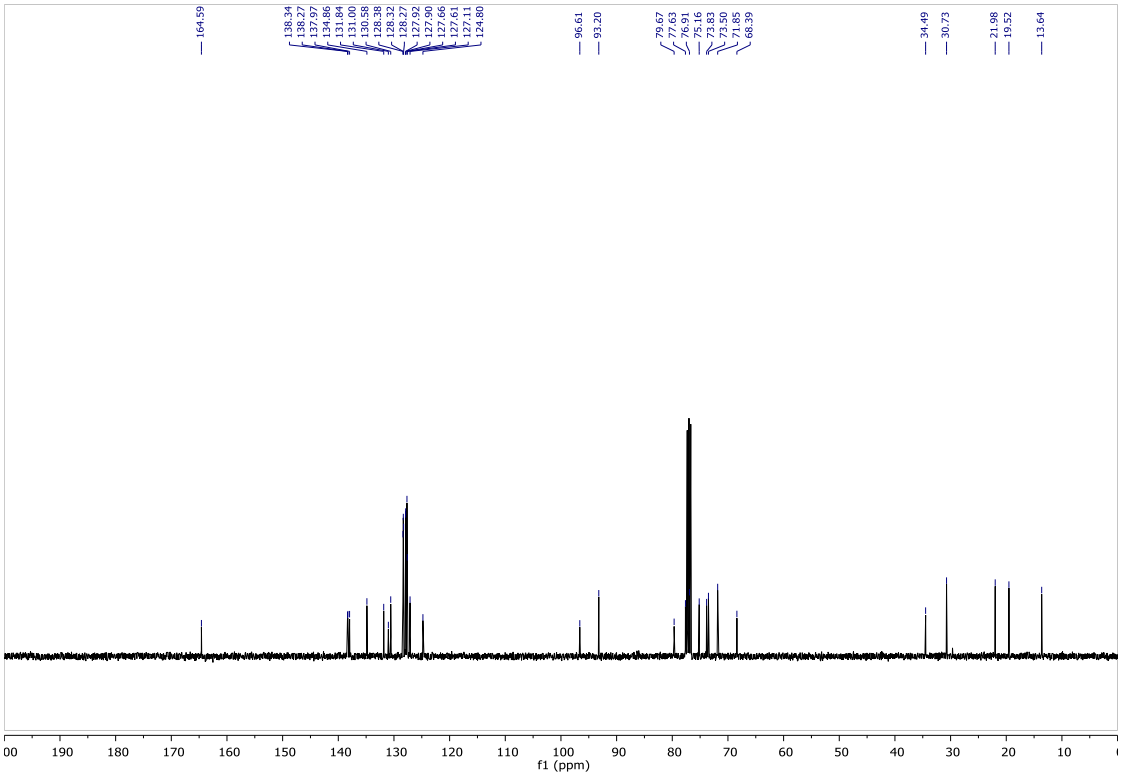

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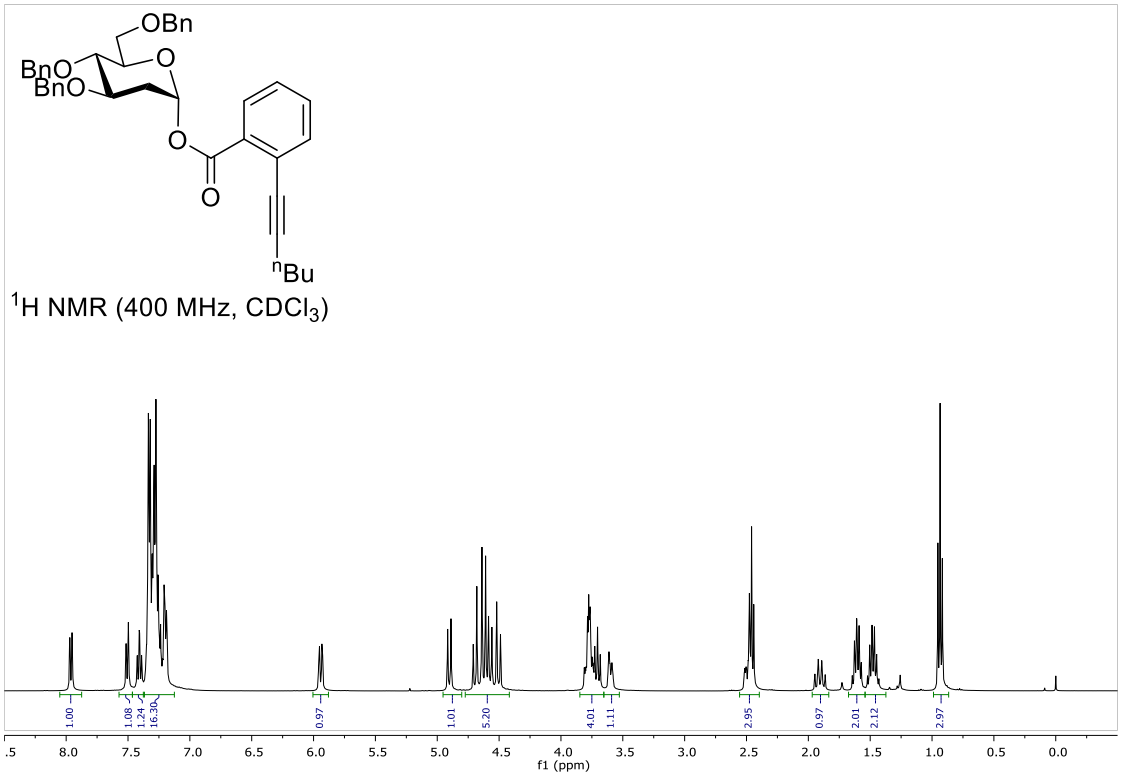


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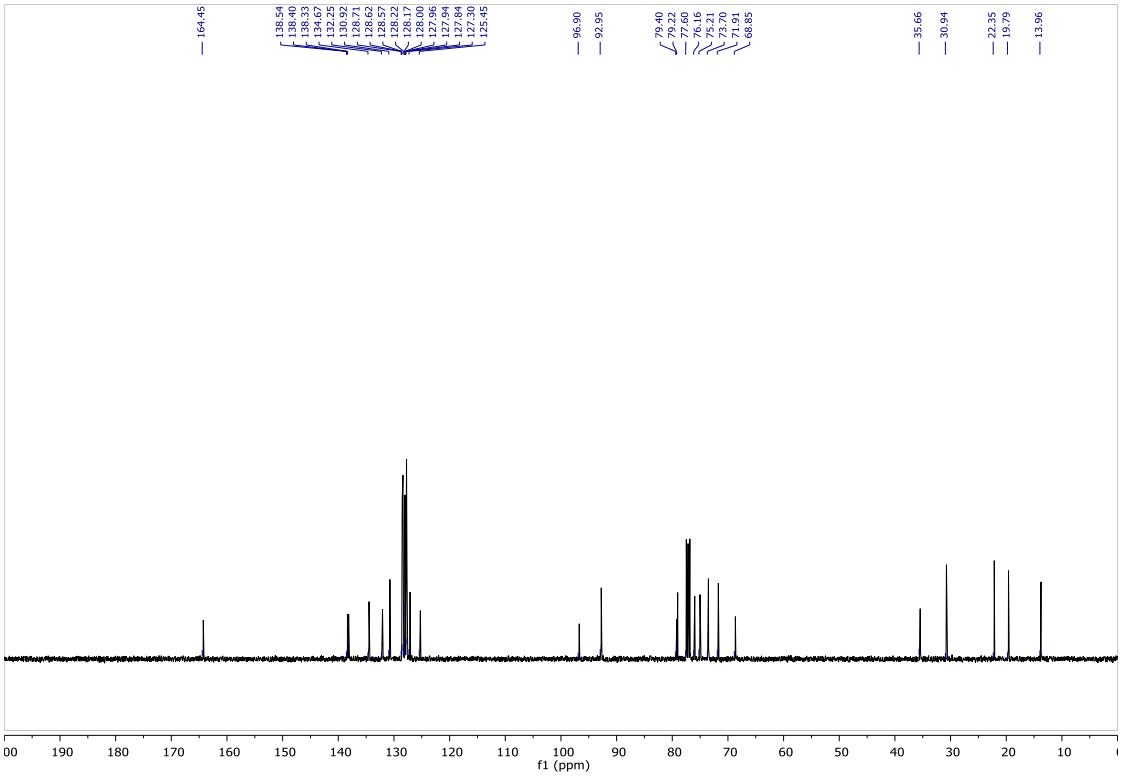

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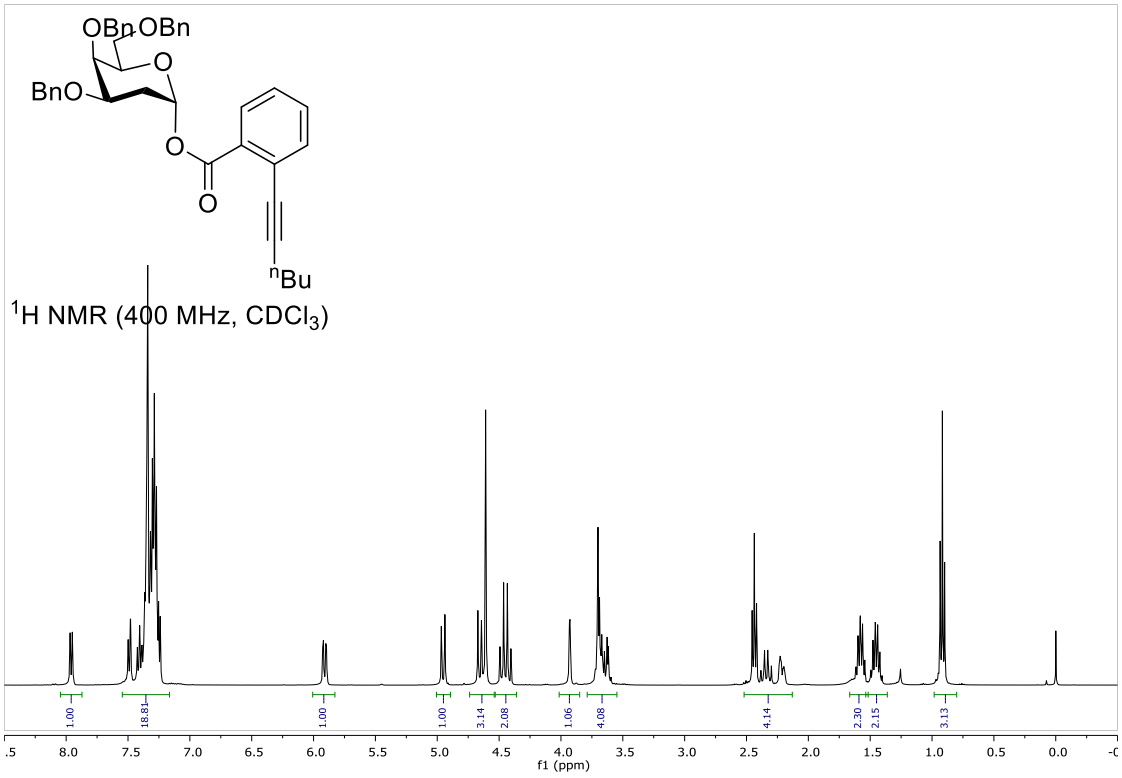


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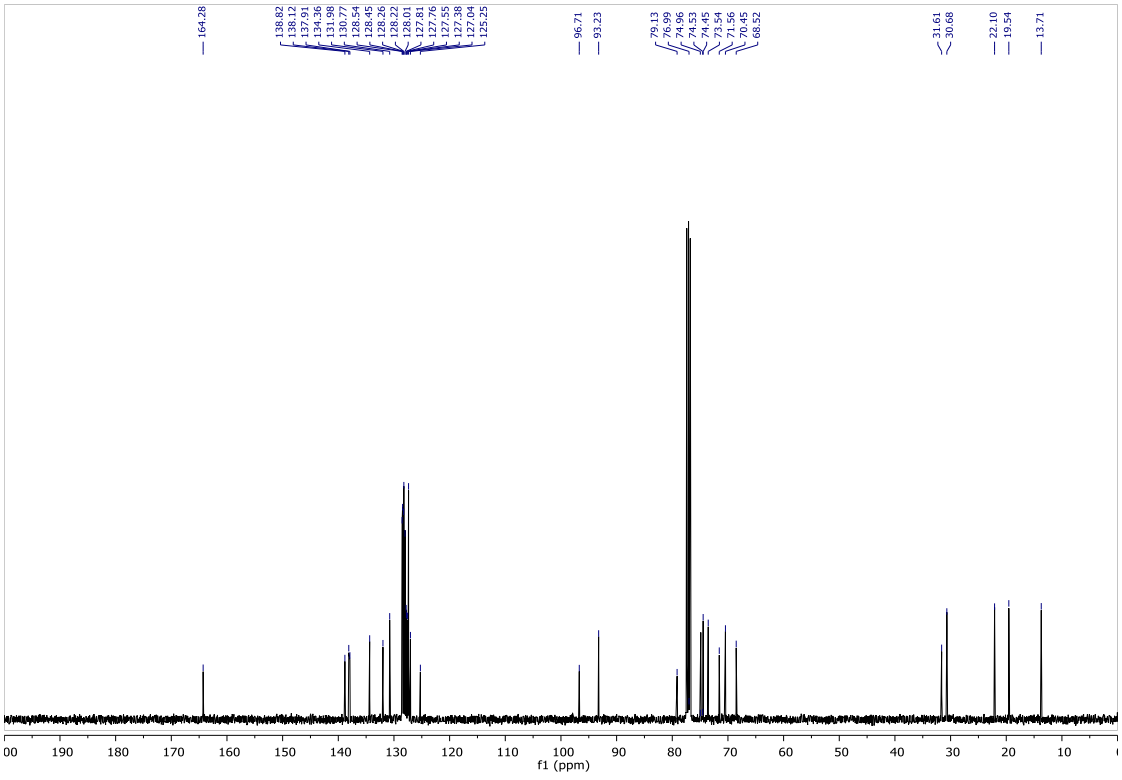

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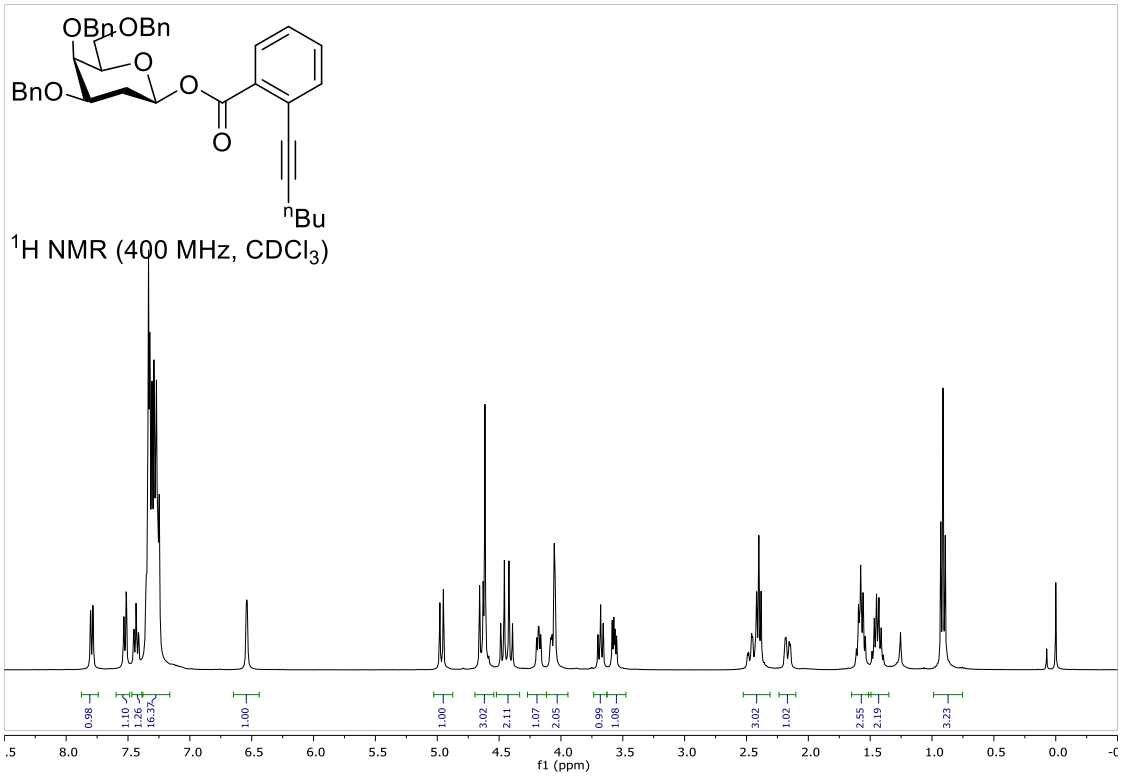


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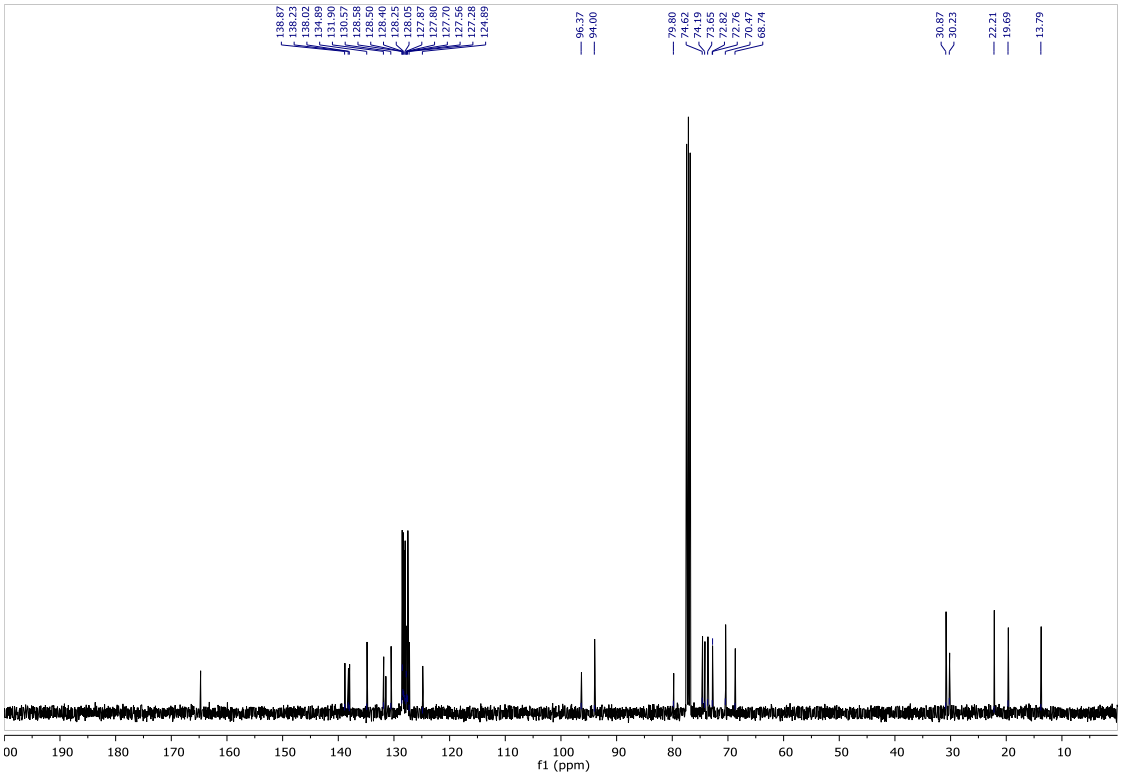

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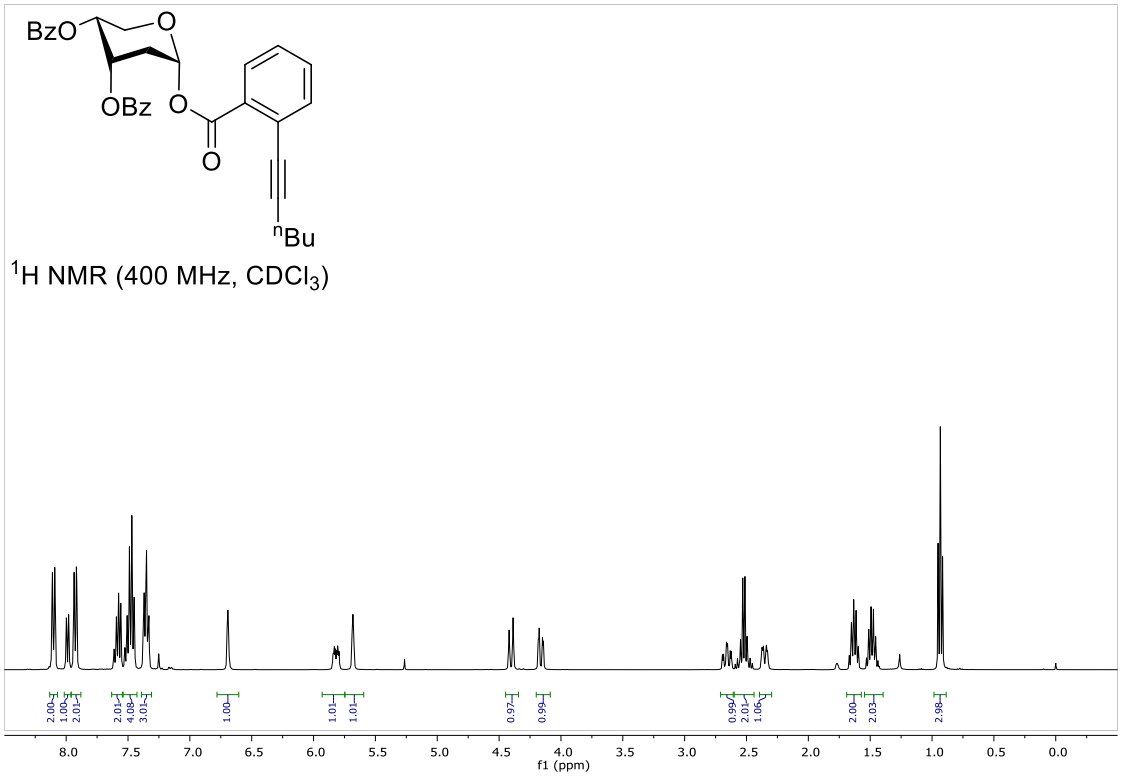


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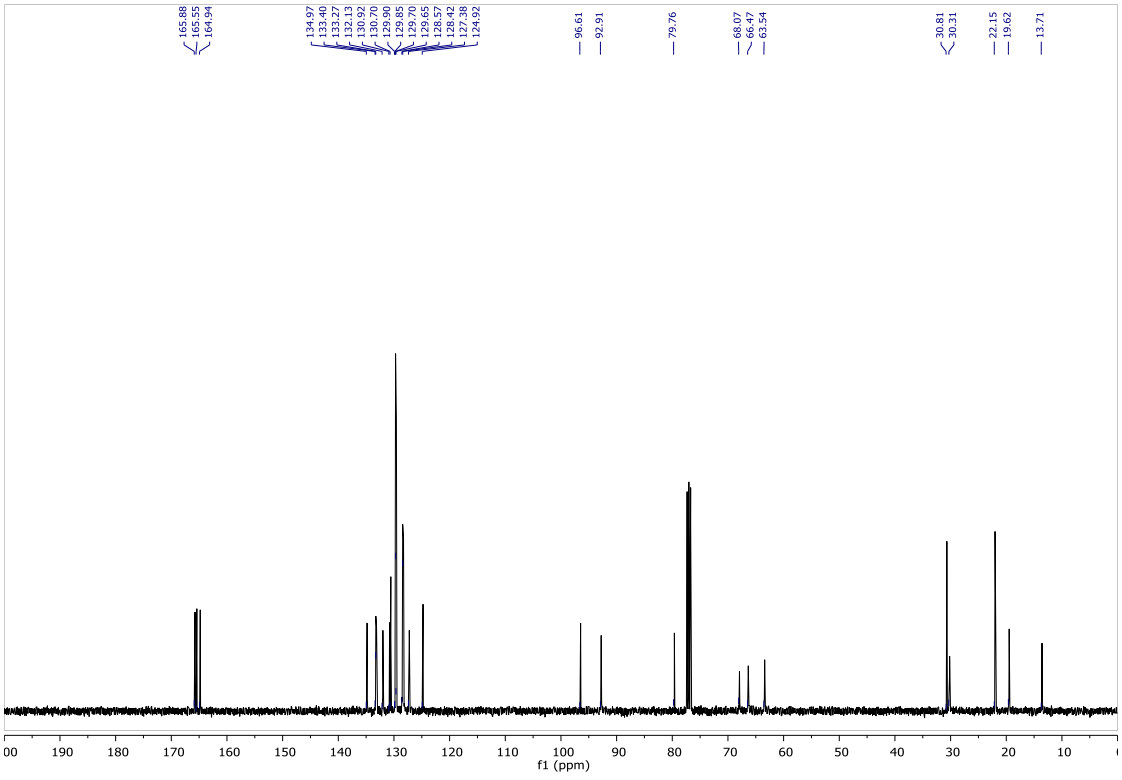

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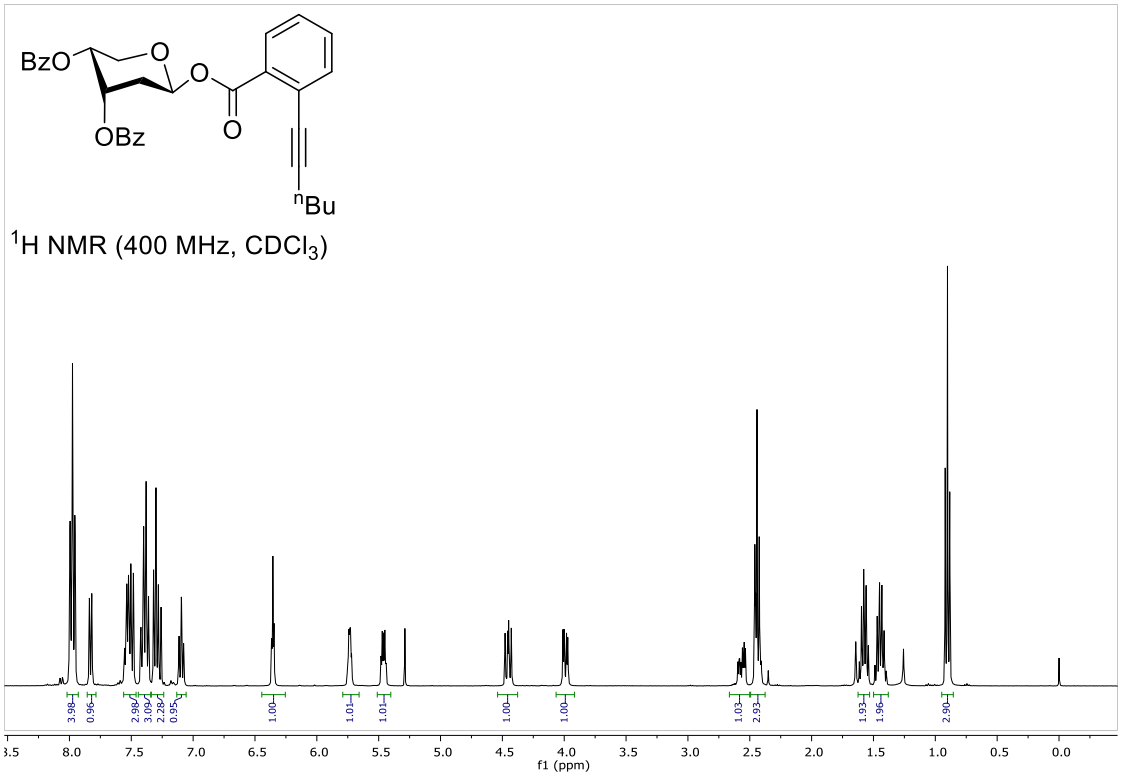


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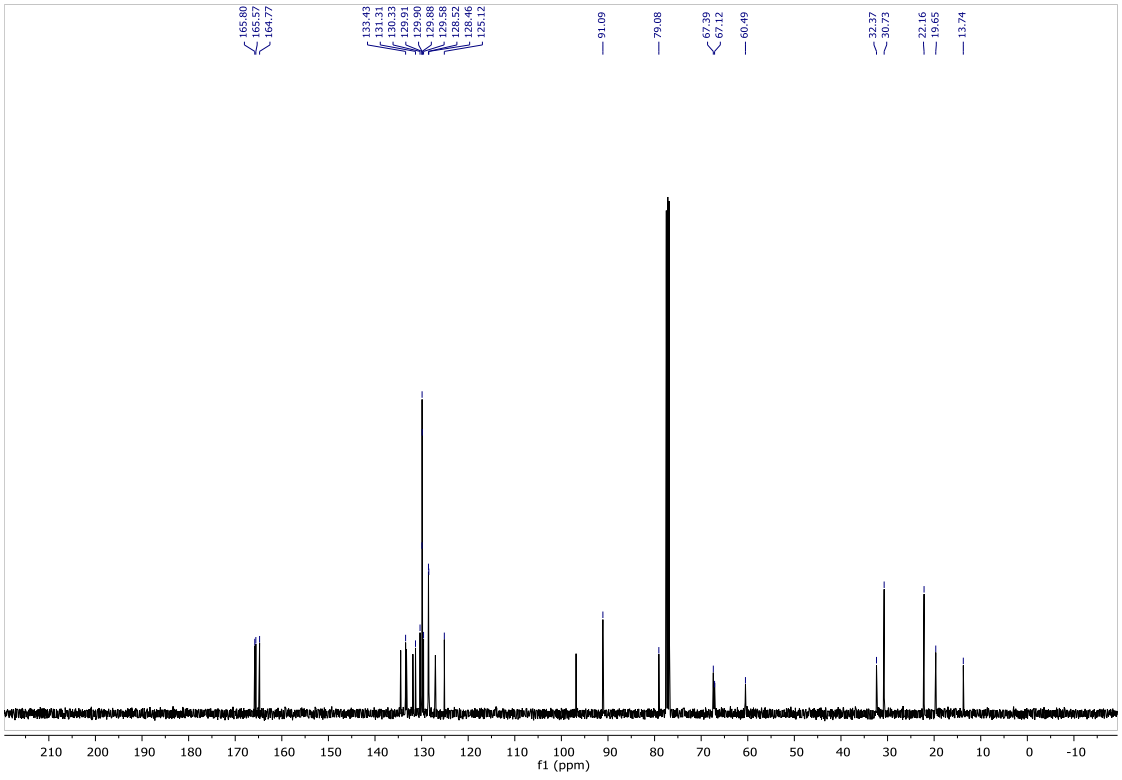

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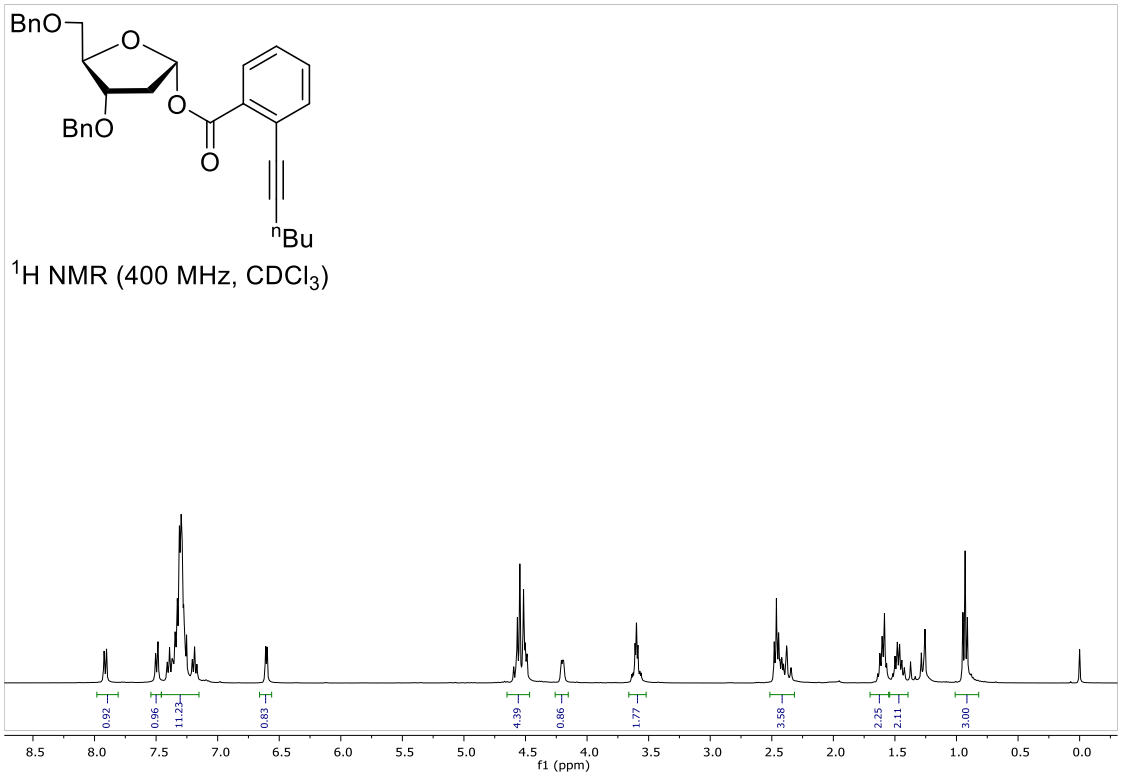


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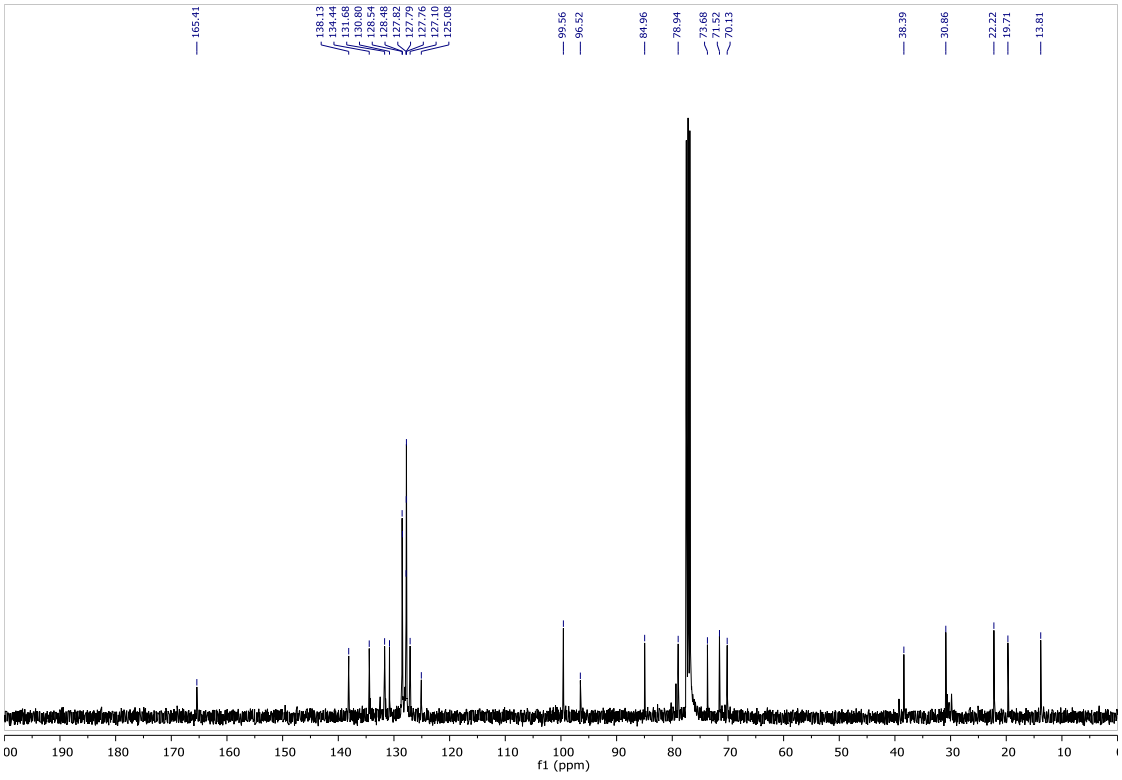

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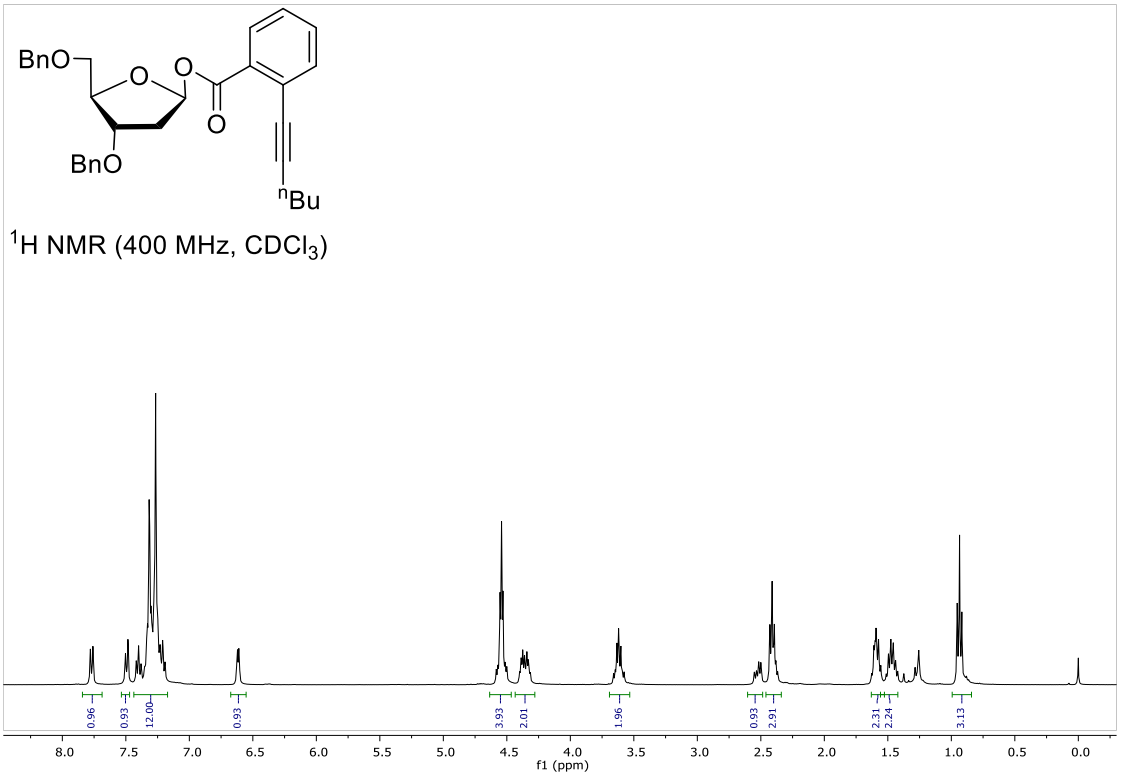


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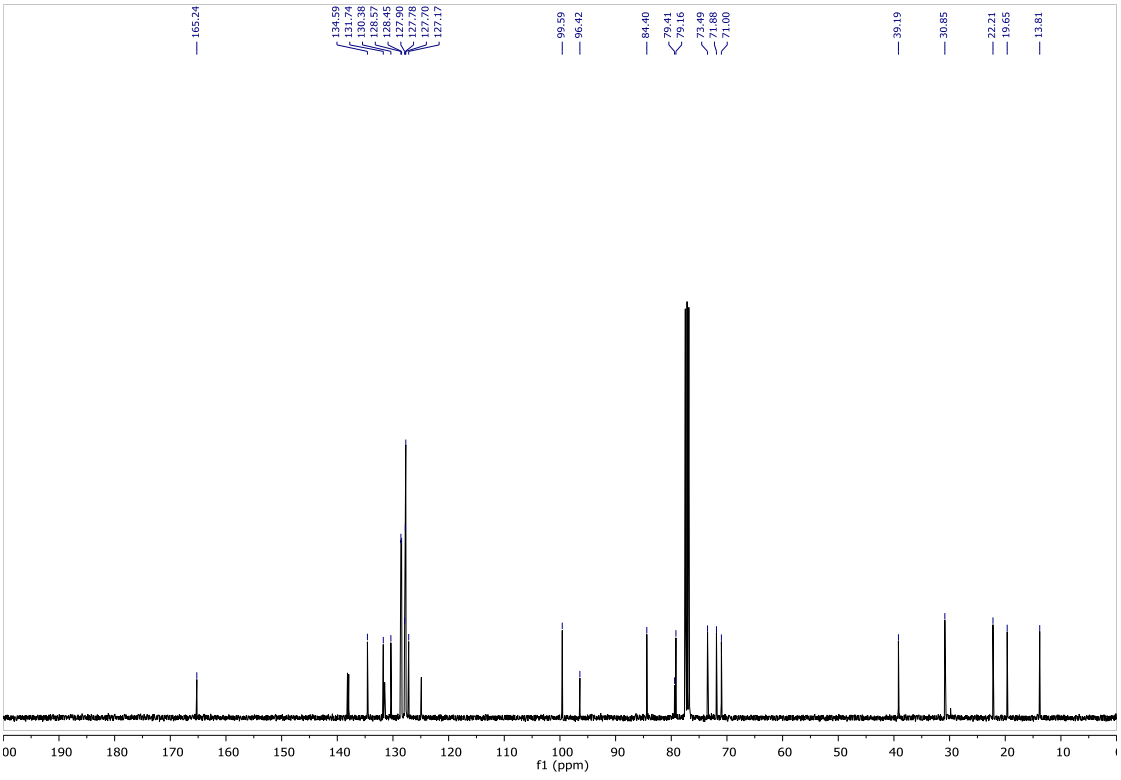
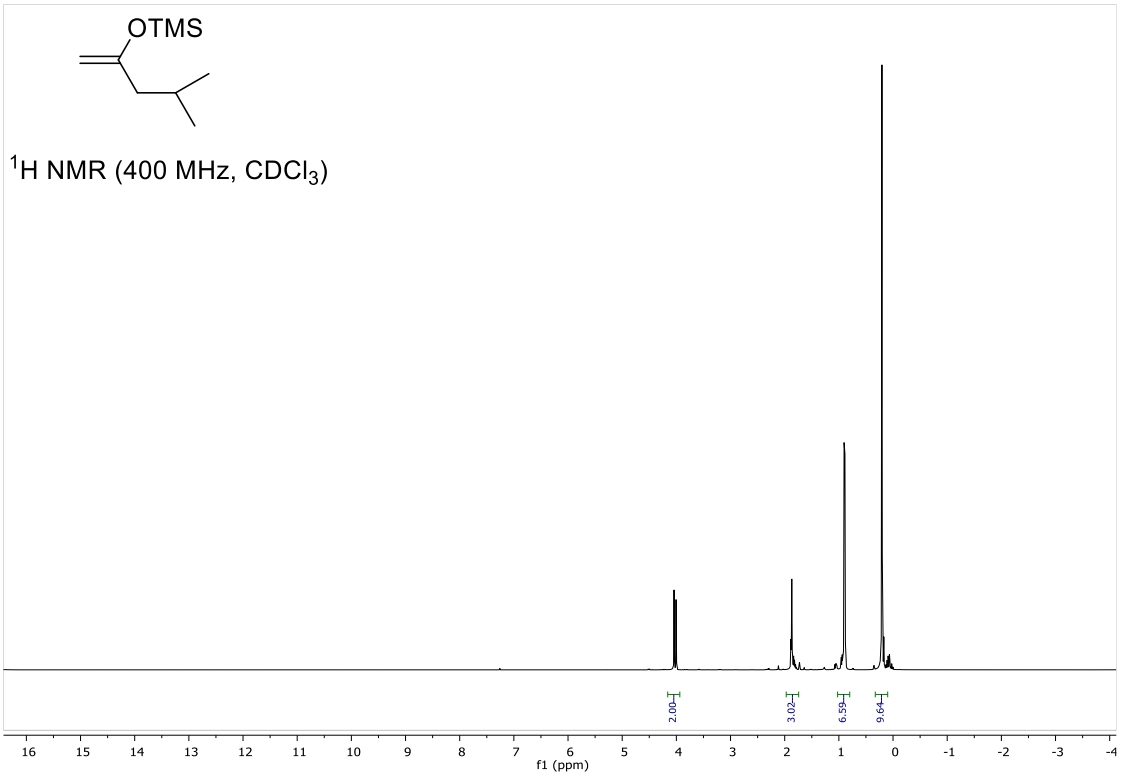
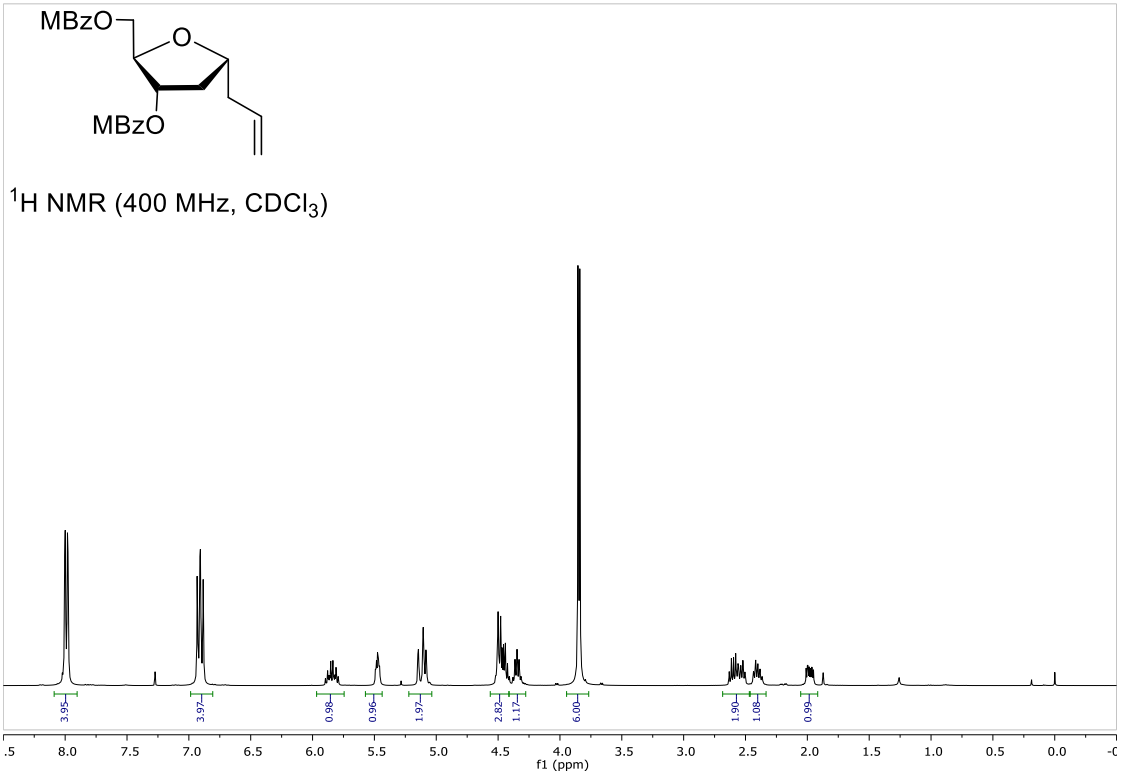


## 4-Methyl-2-trimethylsilyloxy-1-pentene (2d)




## Compound 3c



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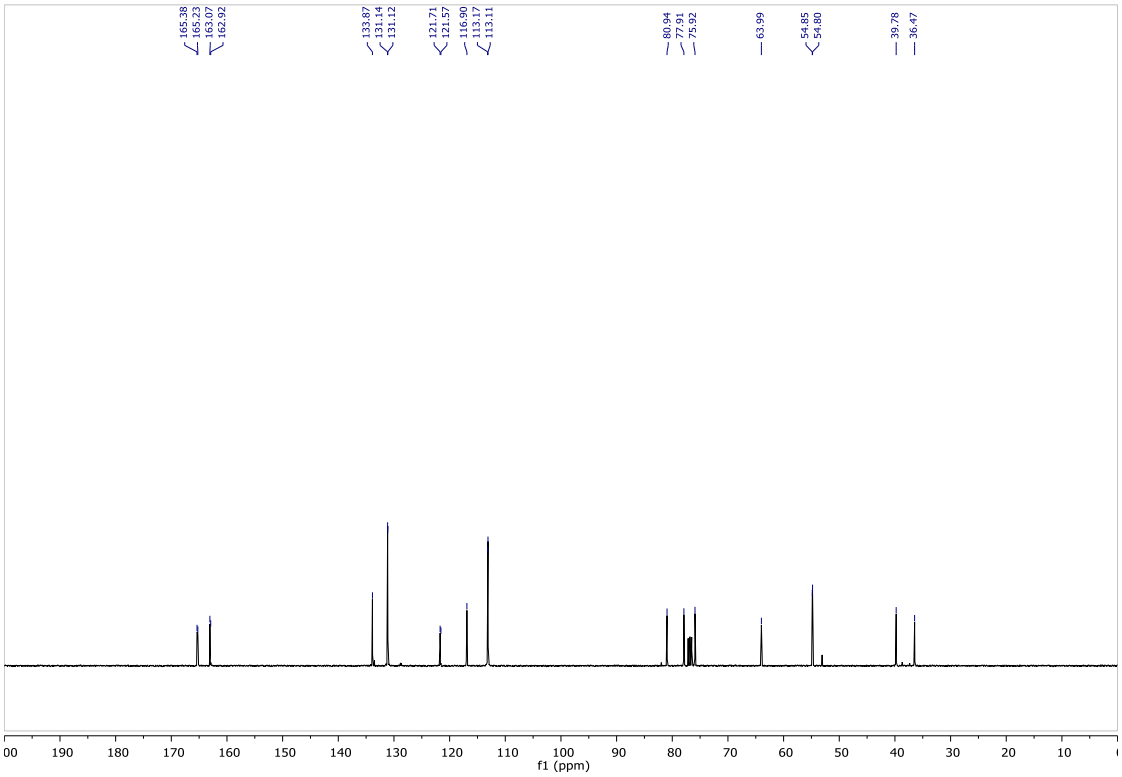


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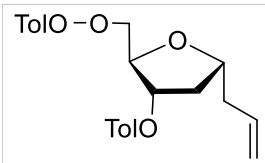


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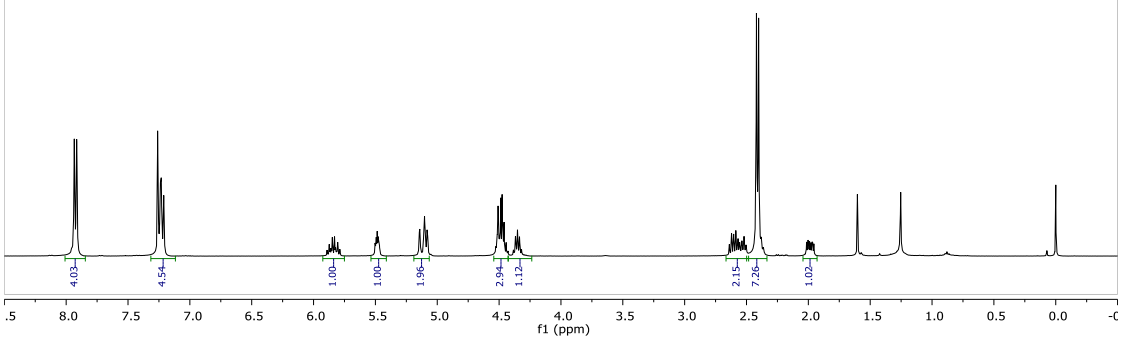

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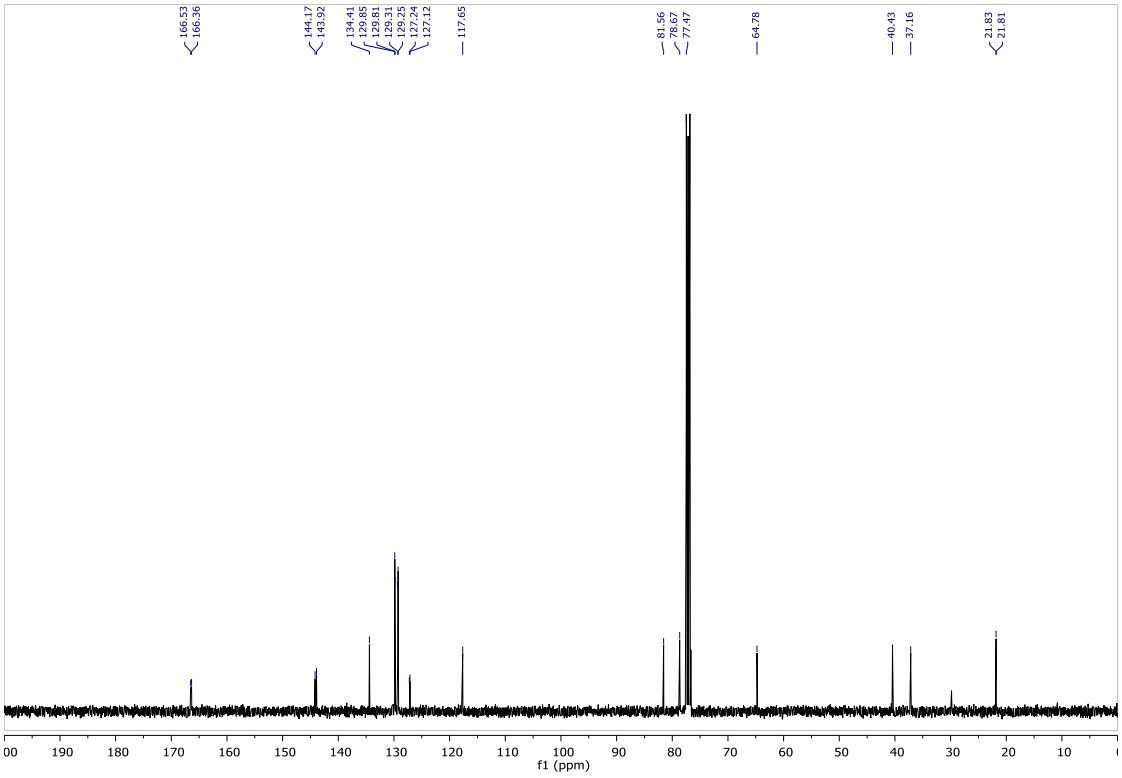


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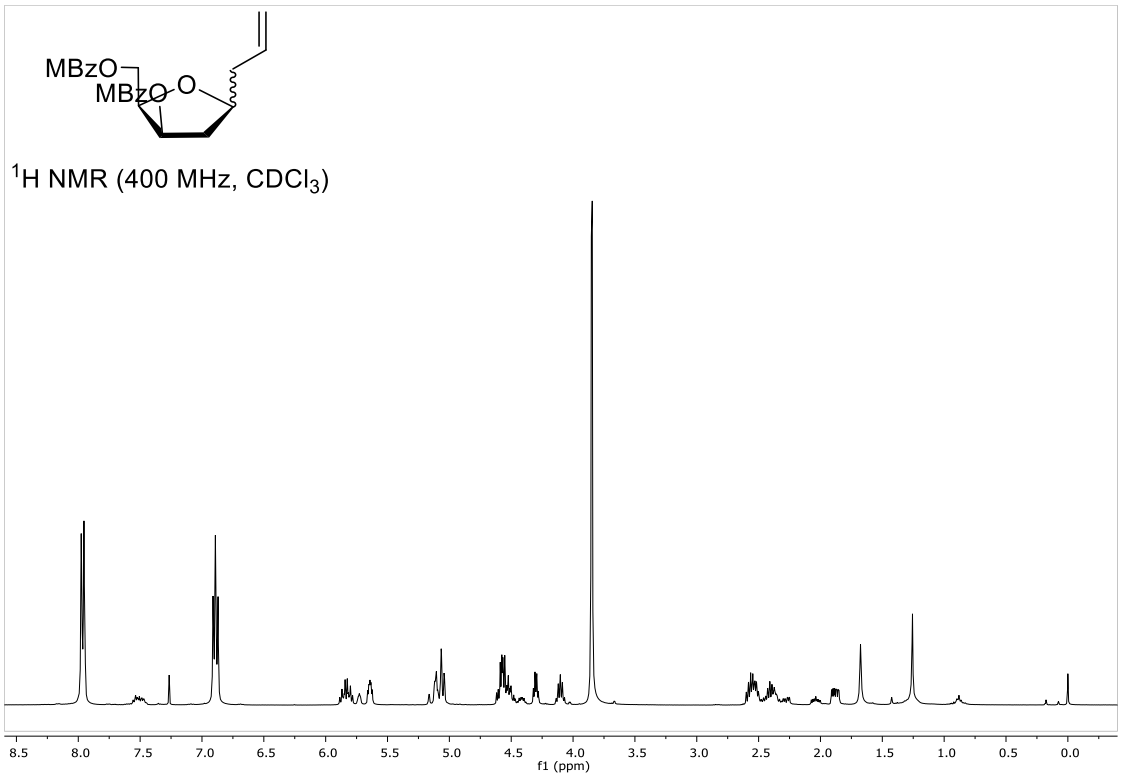
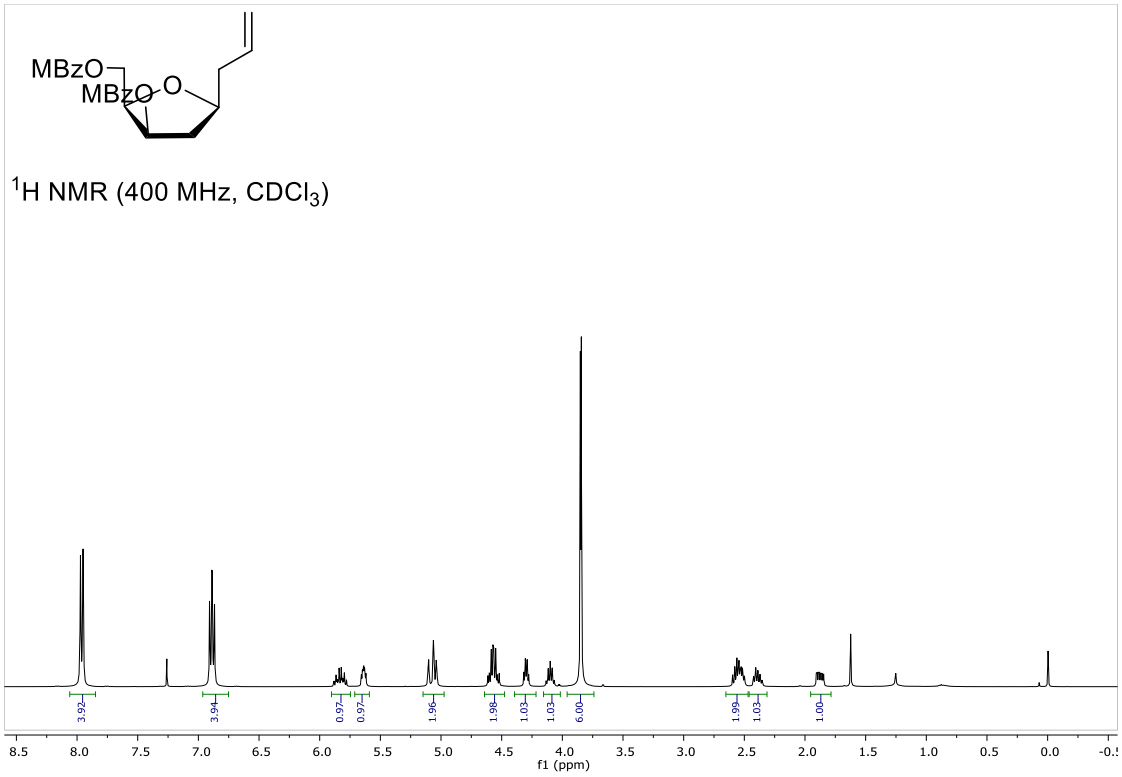


## Compound 3eβ

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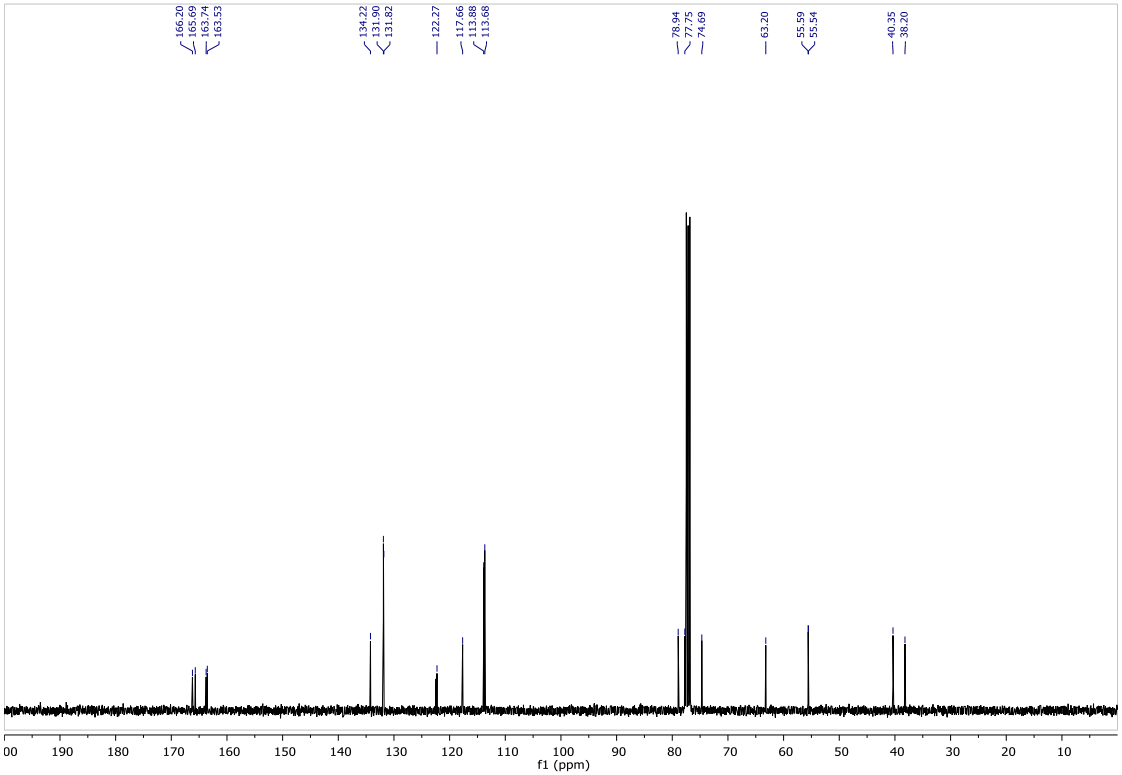

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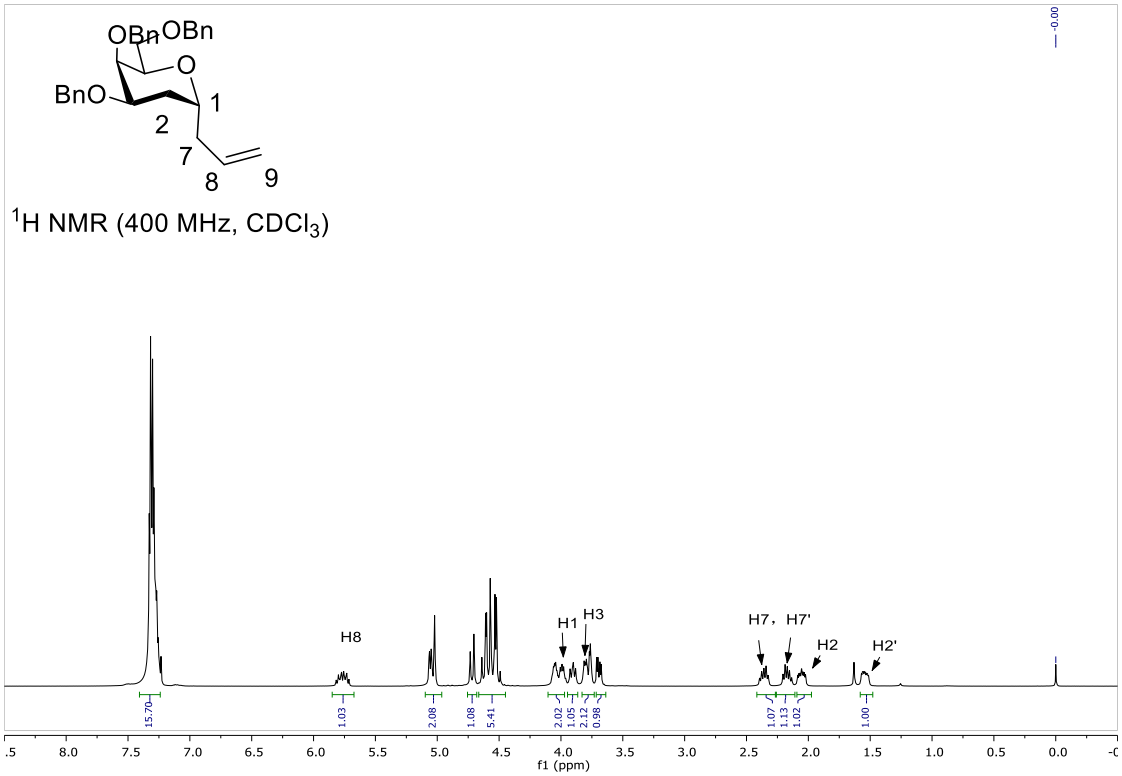


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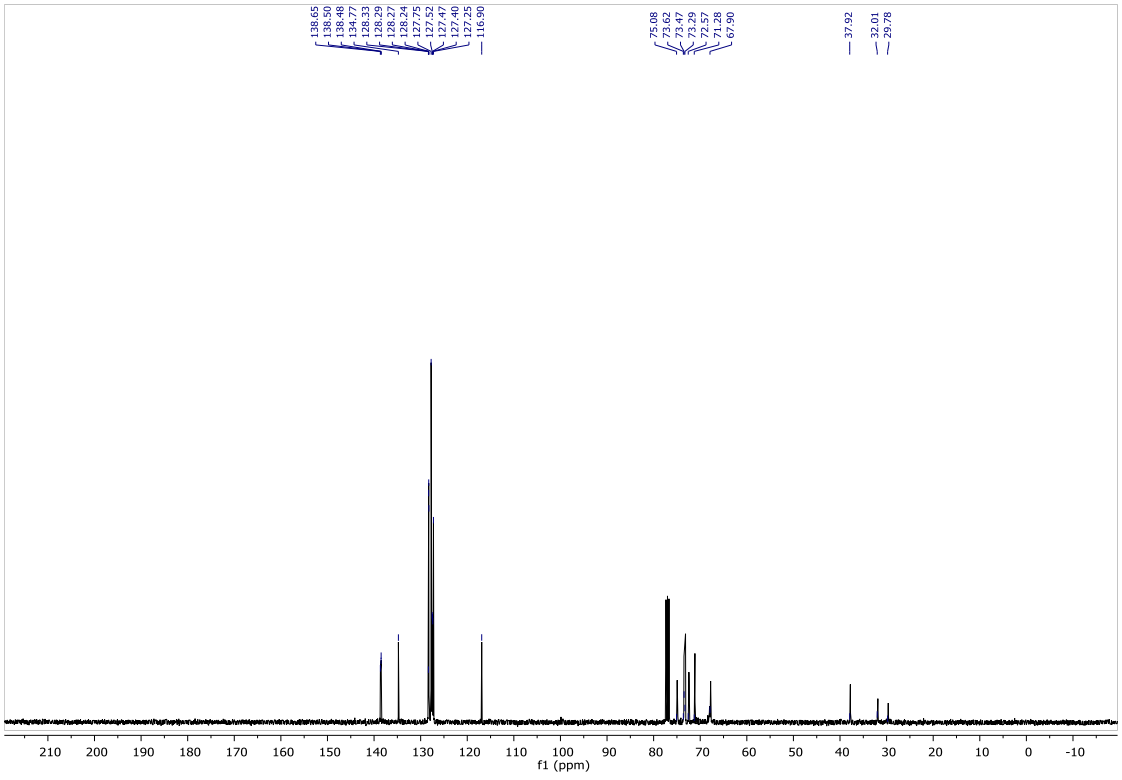
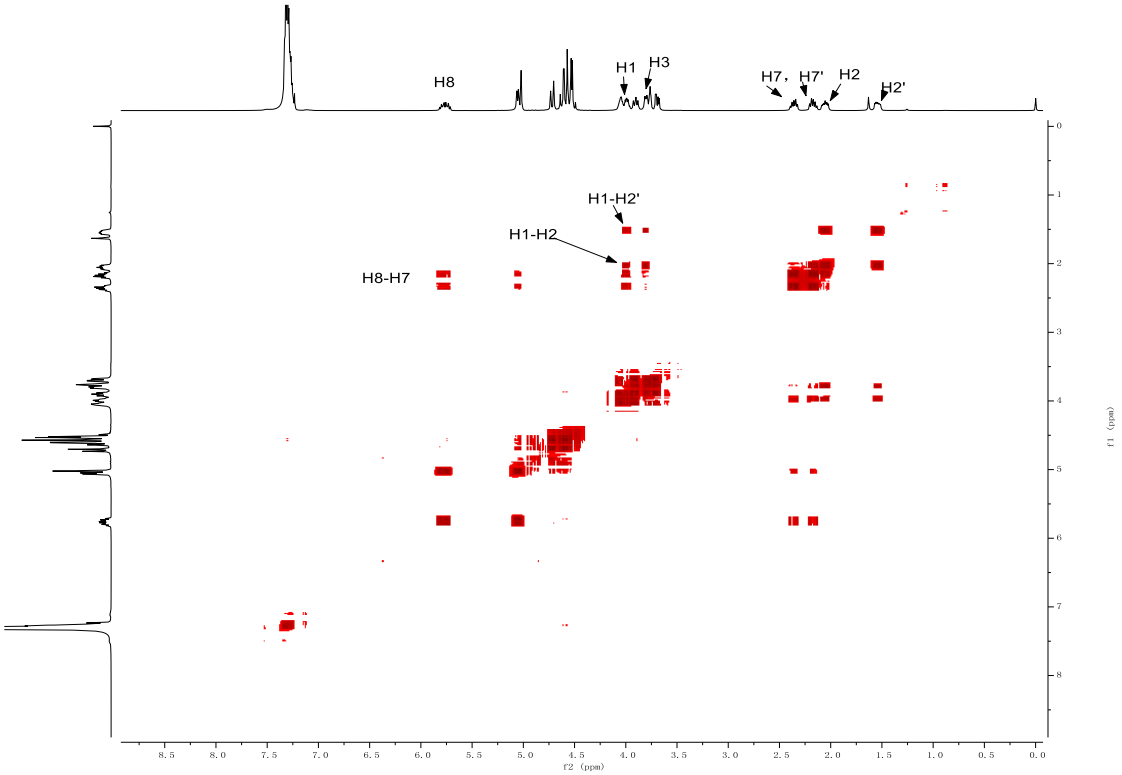


Gcosy NMR (400 MHz, $CDCl_3$)

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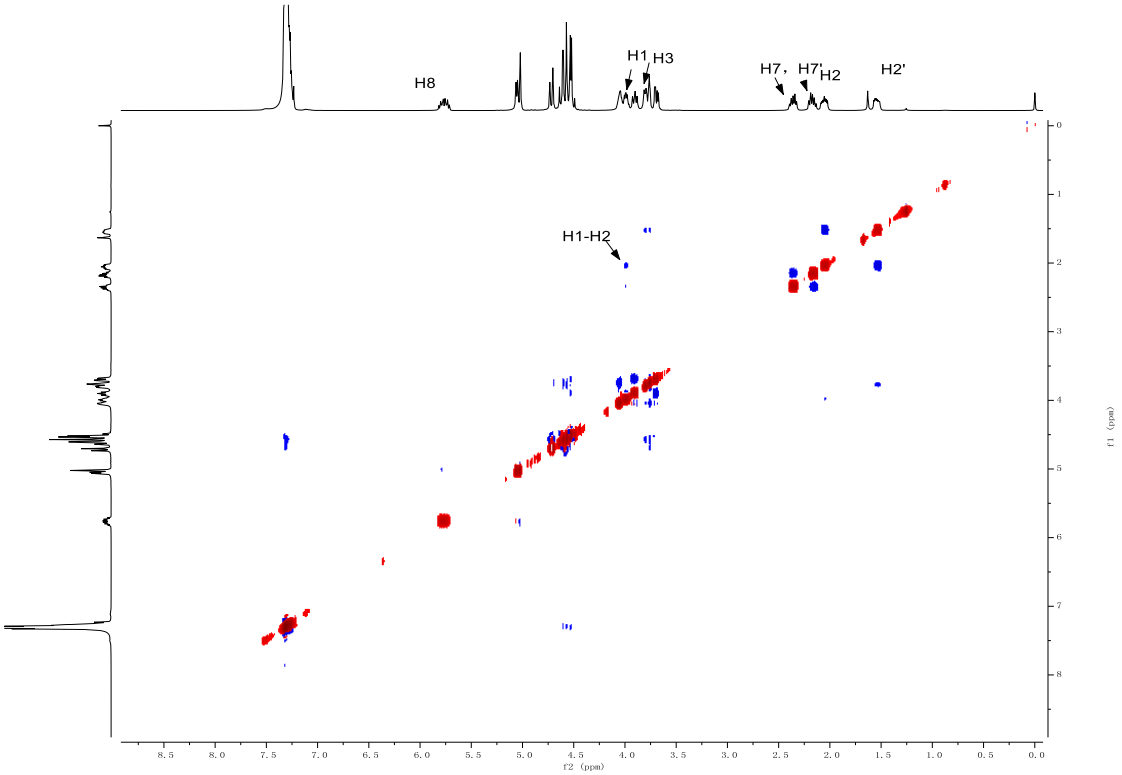
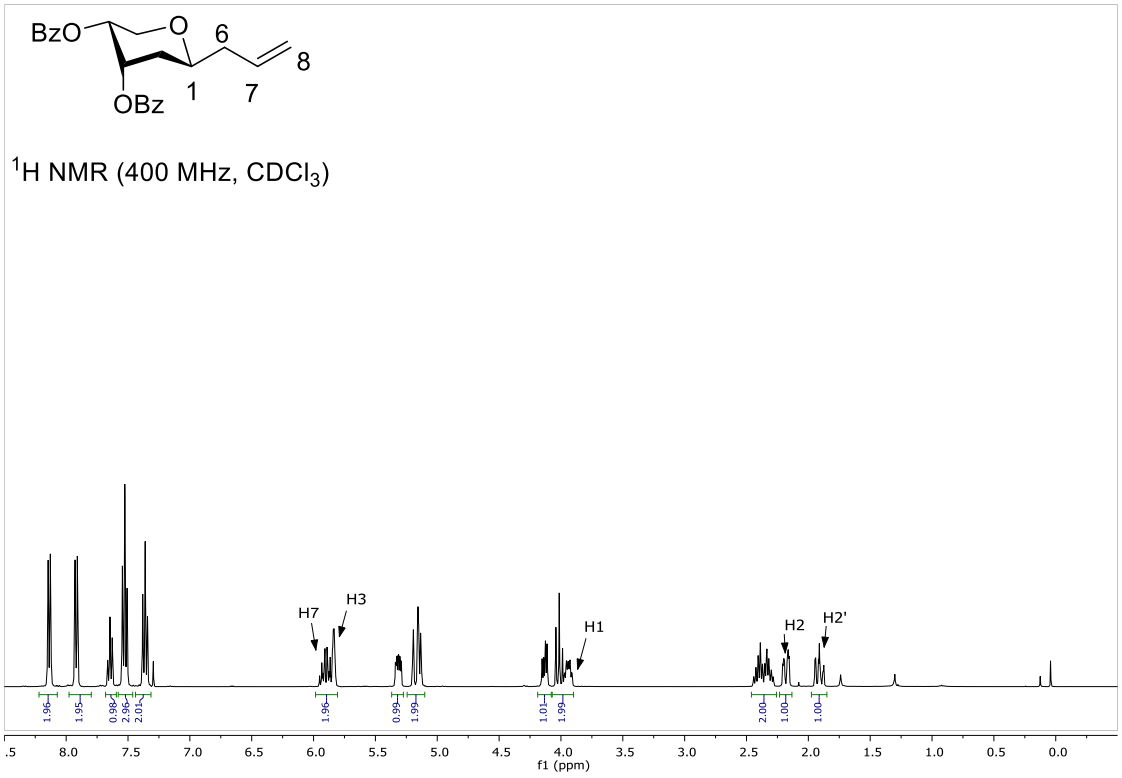
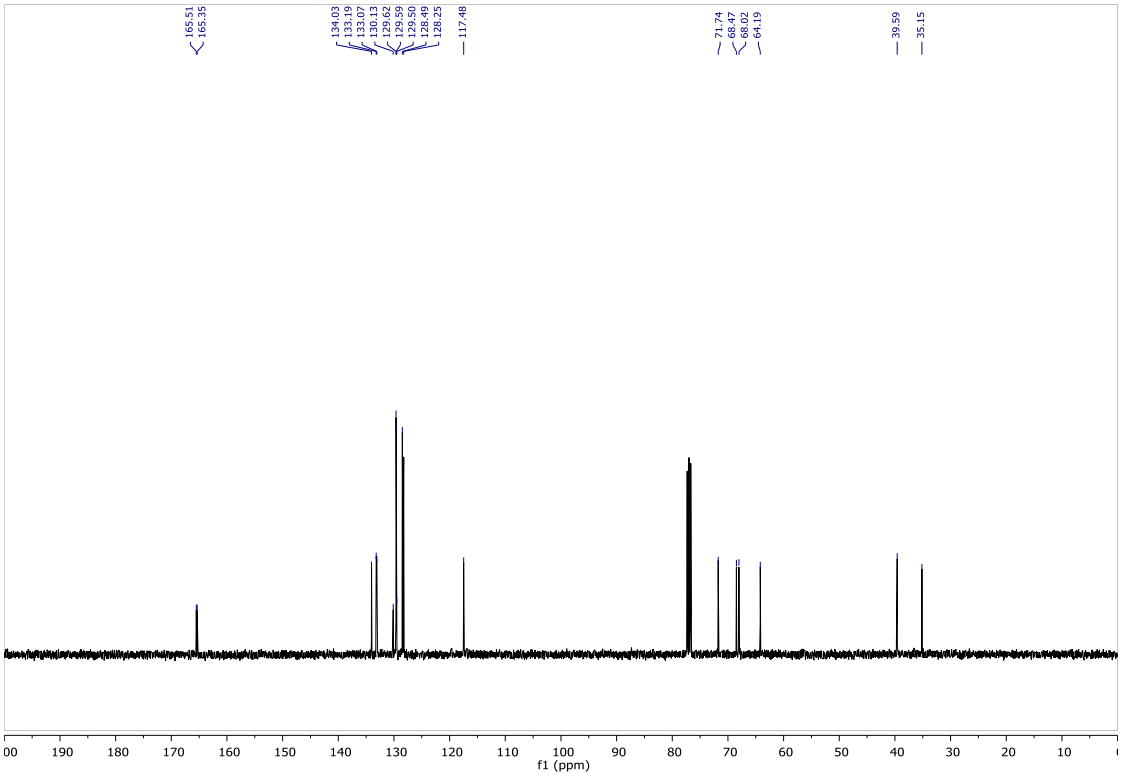


## Compound 3i




$^{1}$H NMR (400 MHz, $CDCl_3$)

$^{13}$C NMR (100 MHz, $CDCl_3$)



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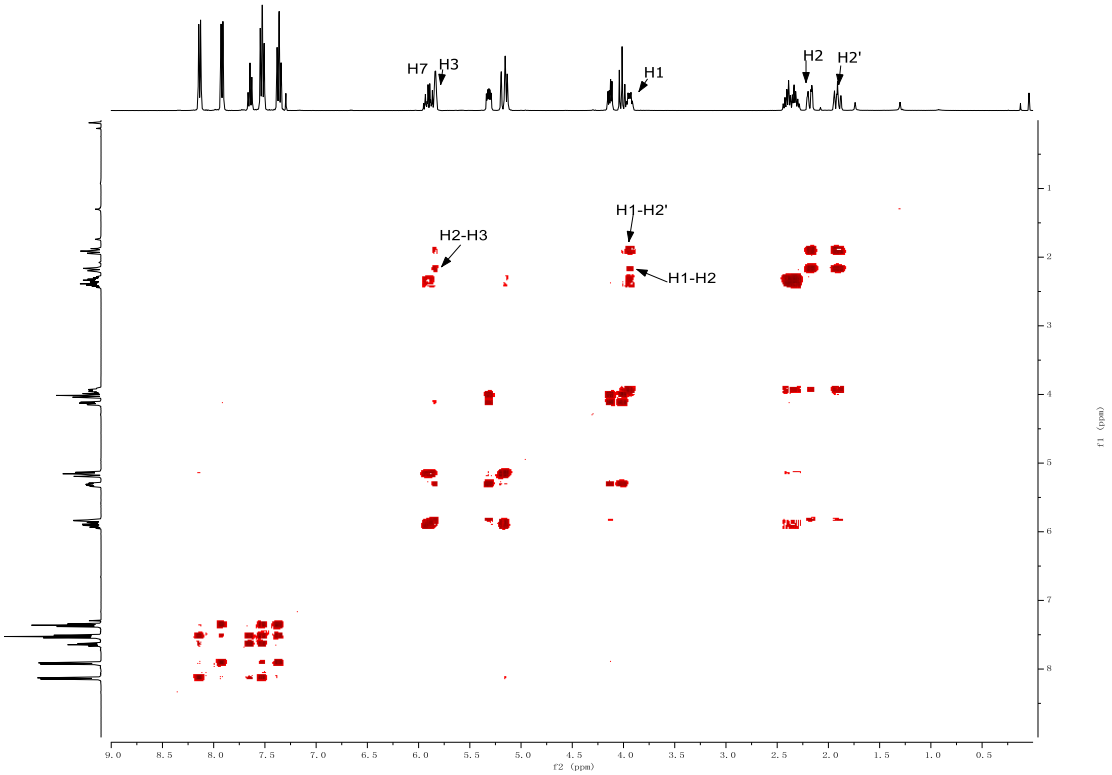


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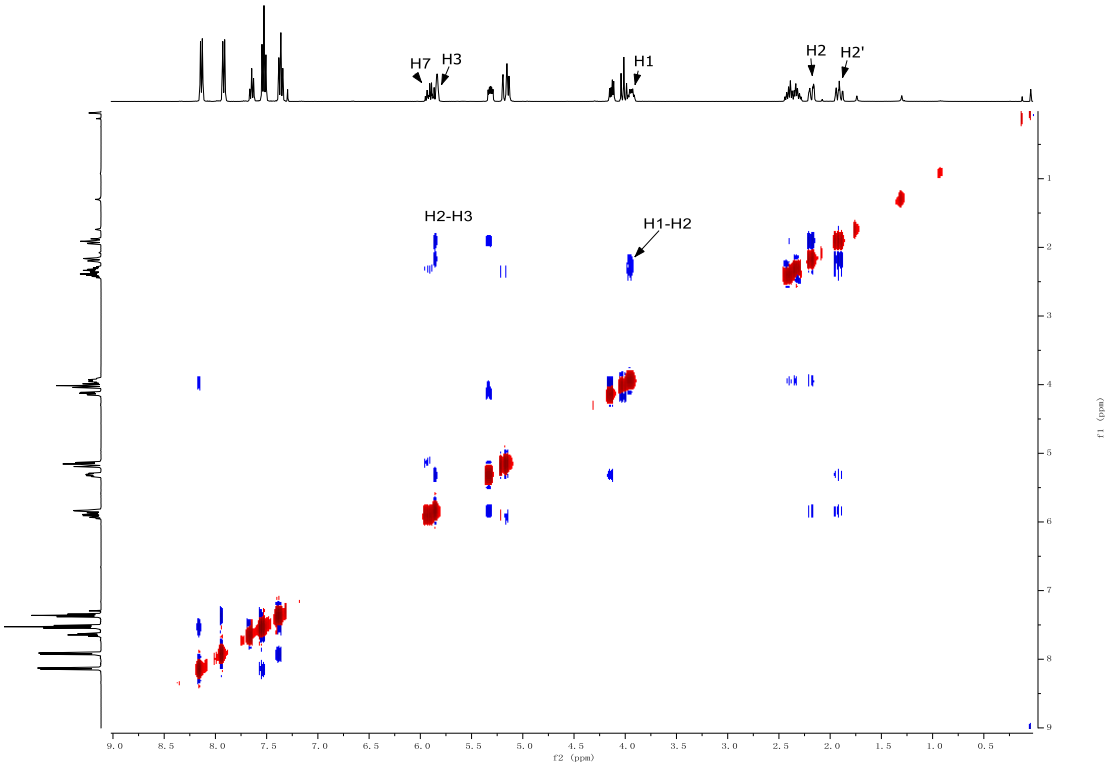
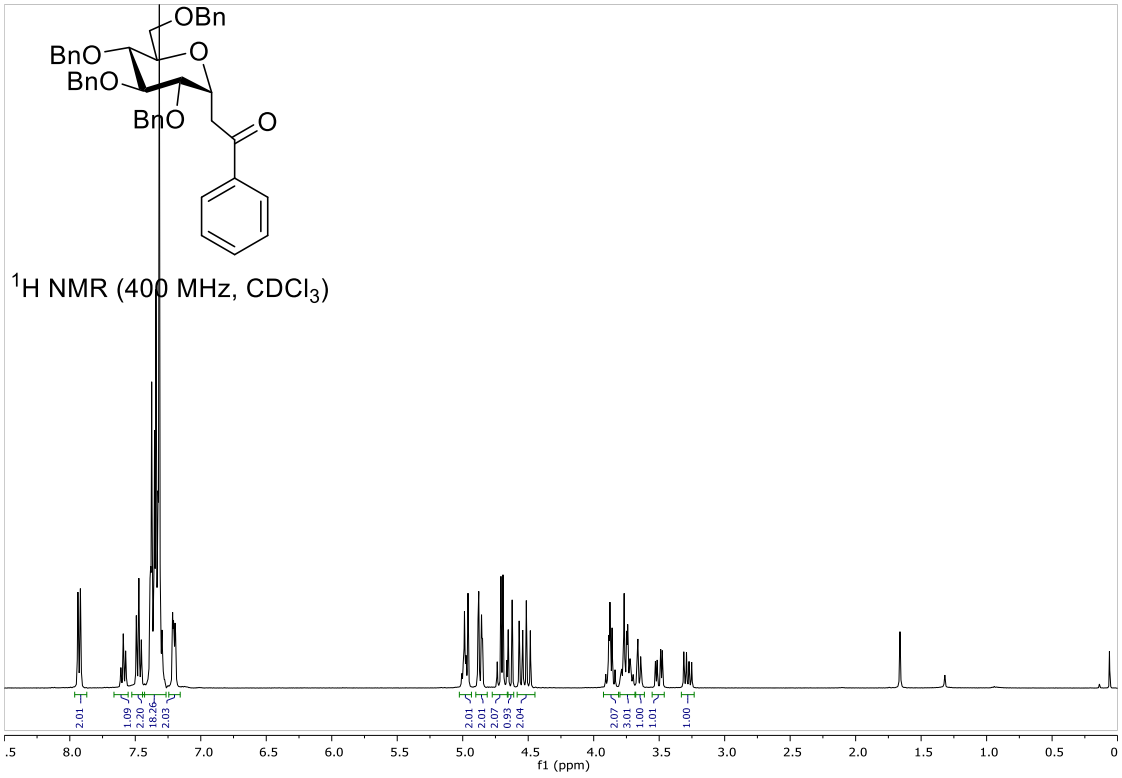
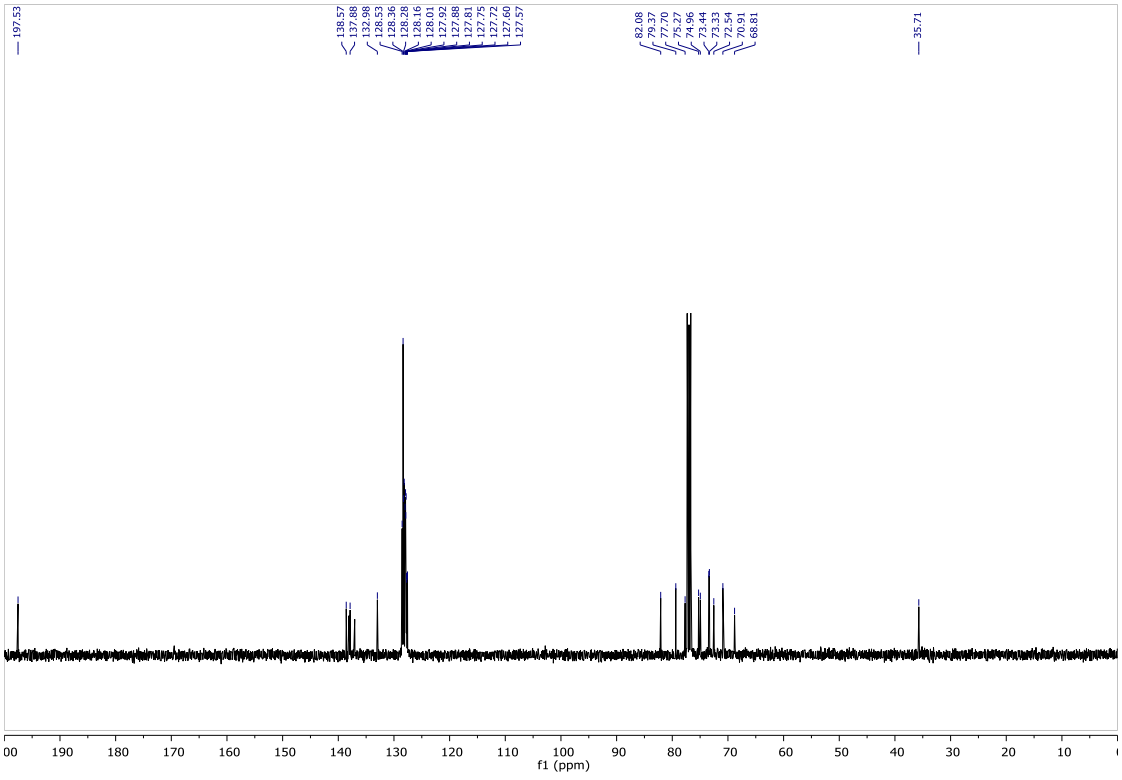


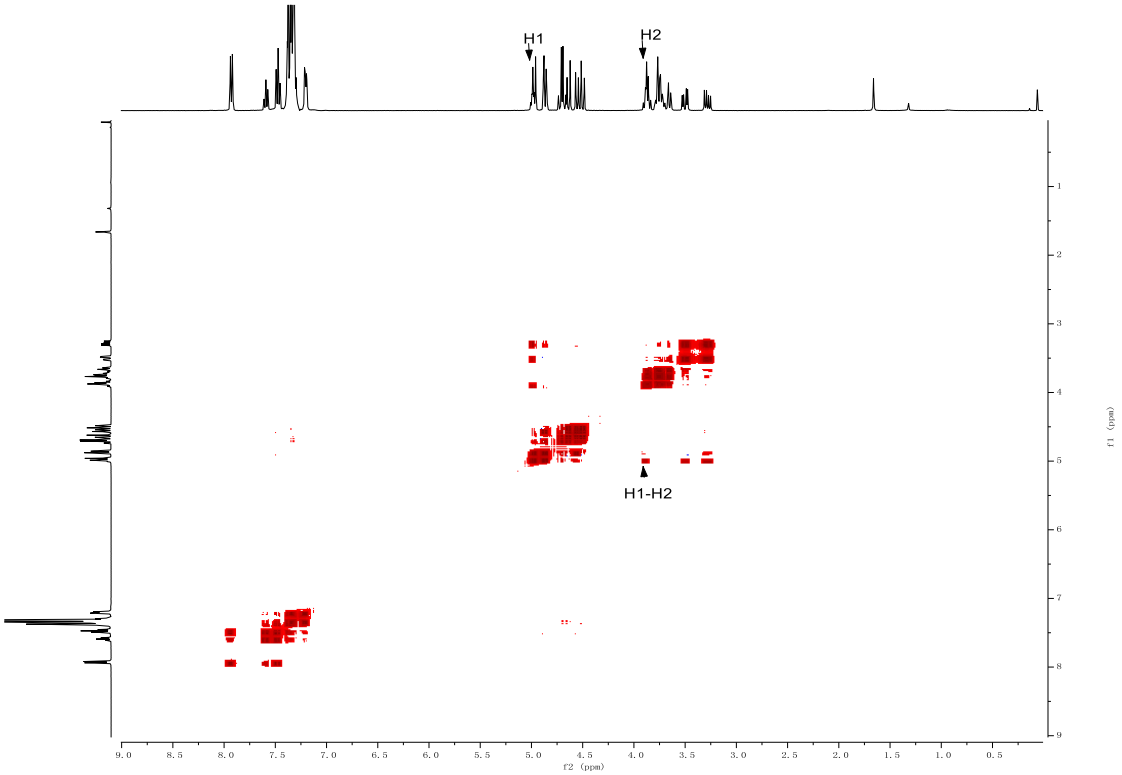
## Compound 4aα



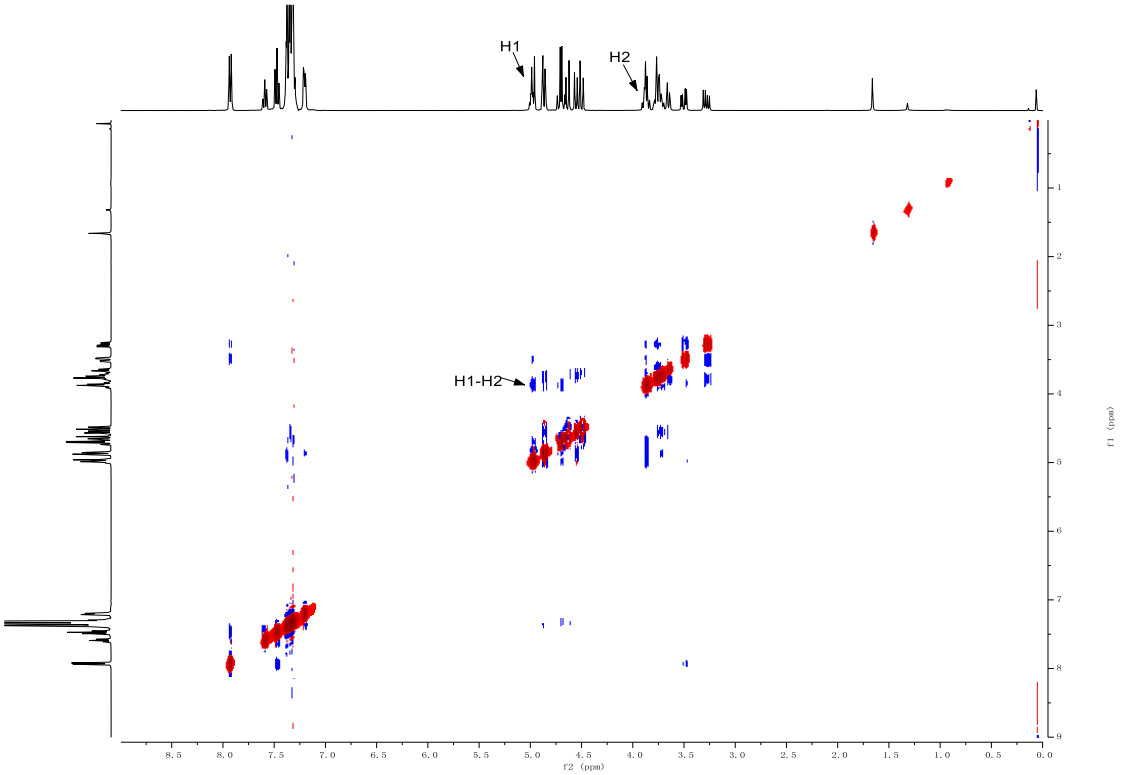

$^{13}C$ NMR (100 MHz, $CDCl_3$)



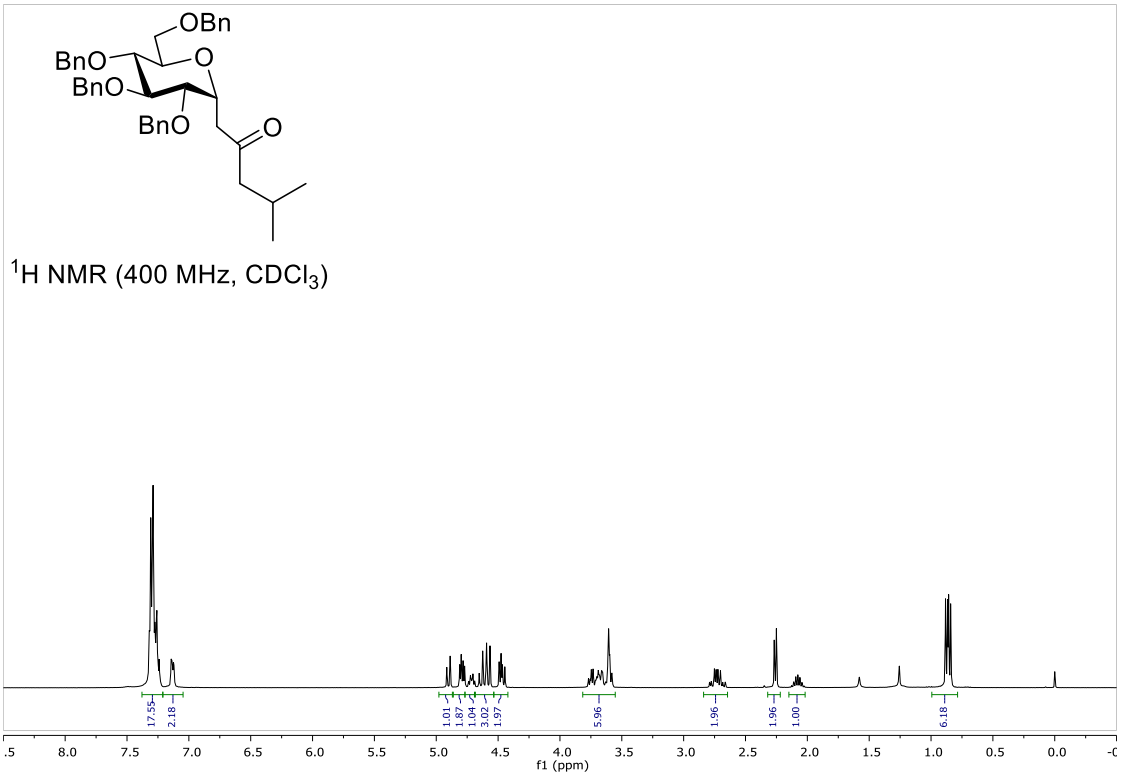
Gcosy NMR (400 MHz, $CDCl_3$)



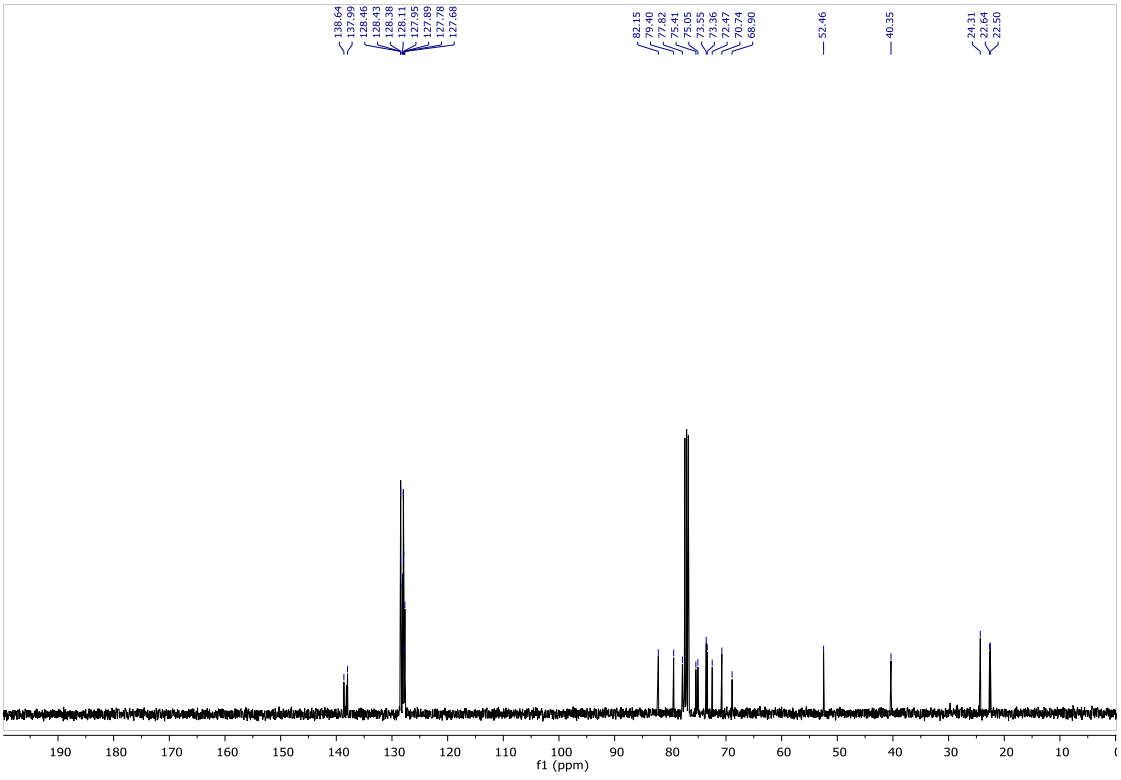

Noesy NMR (400 MHz, $CDCl_3$)



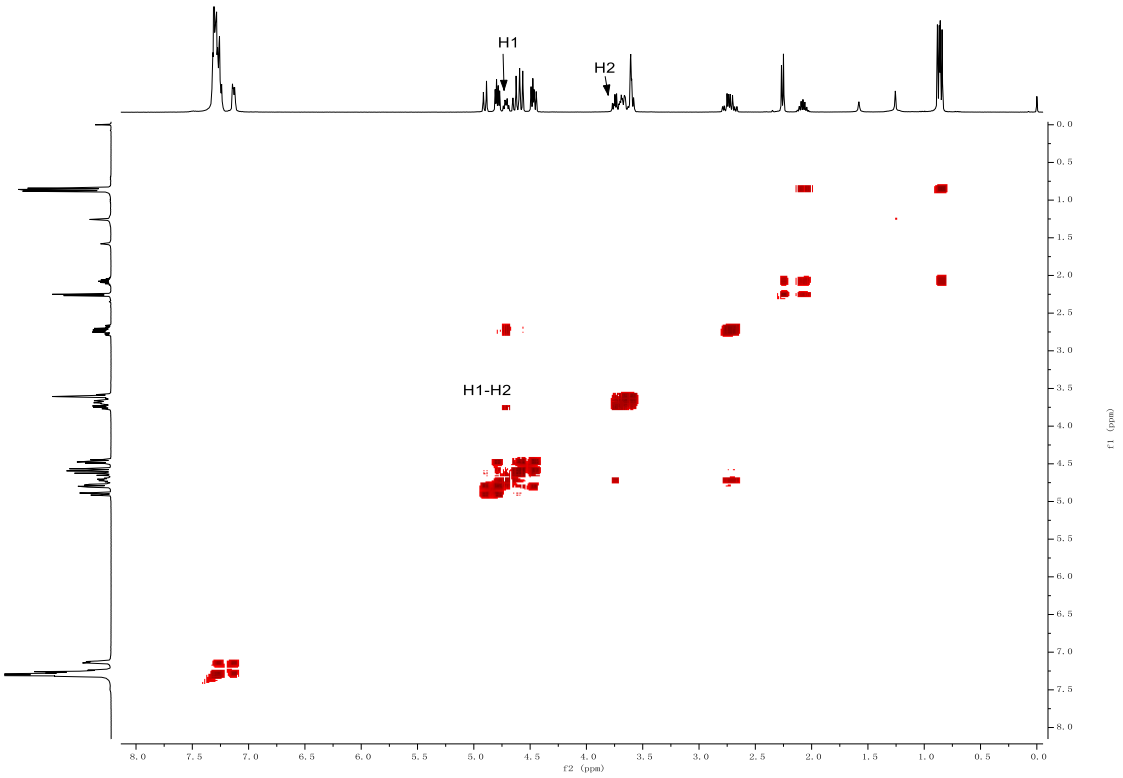
## Compound 4bα



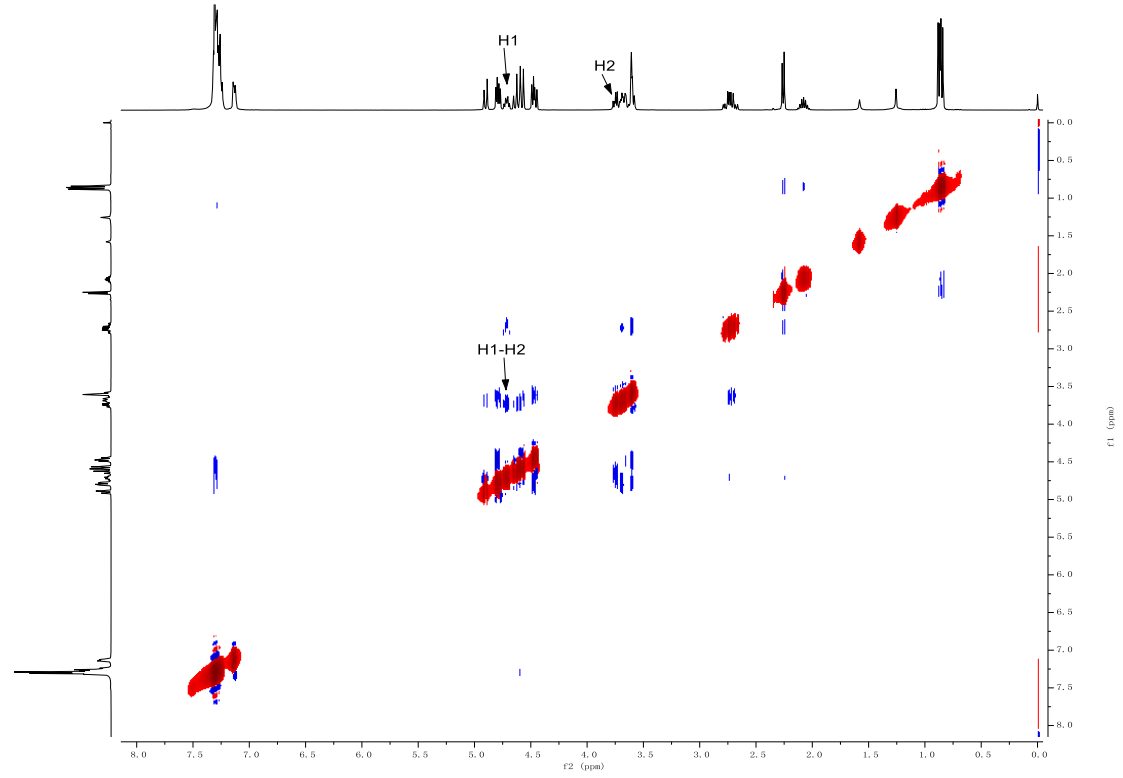

$^{13}$C NMR (100 MHz, $CDCl_3$)



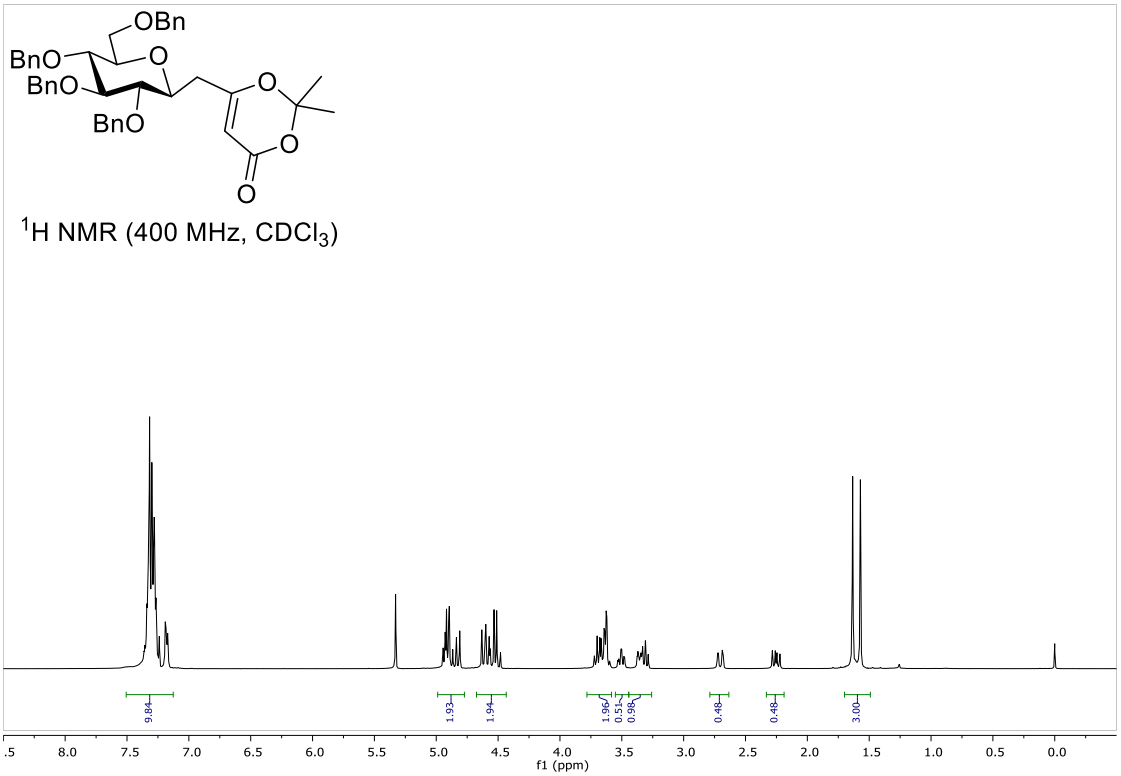
Gcosy NMR (400 MHz, $CDCl_3$)



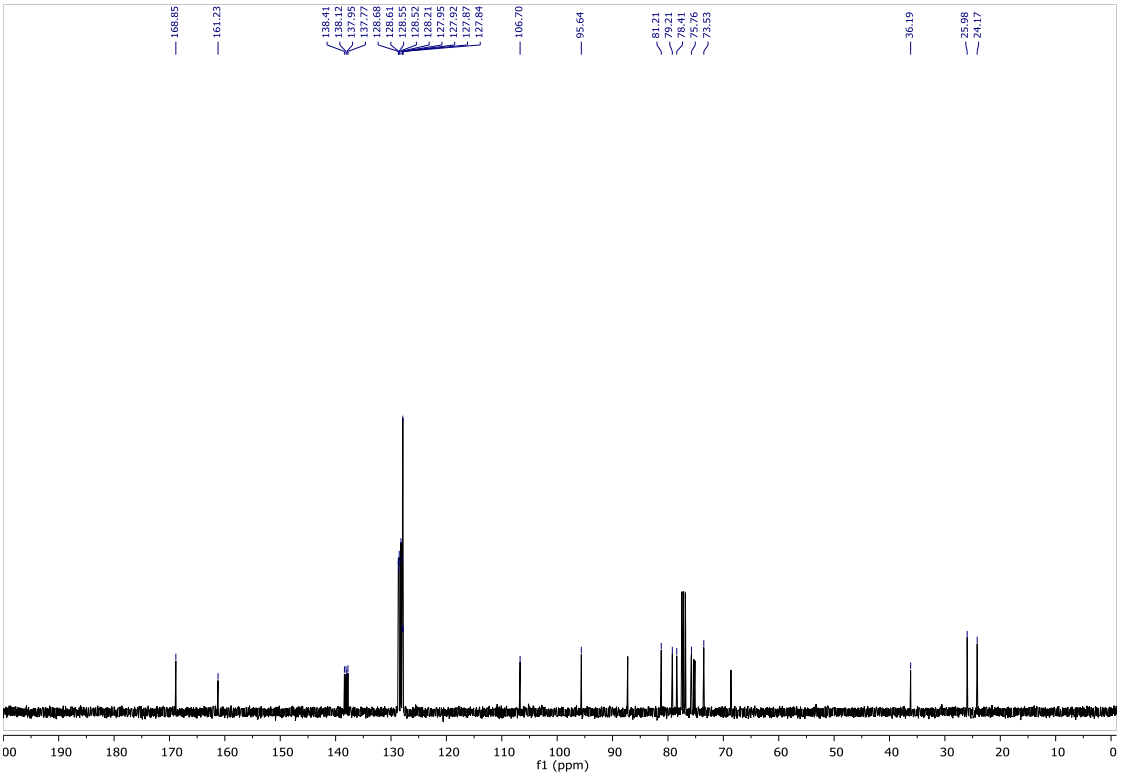

Noesy NMR (400 MHz, $CDCl_3$)



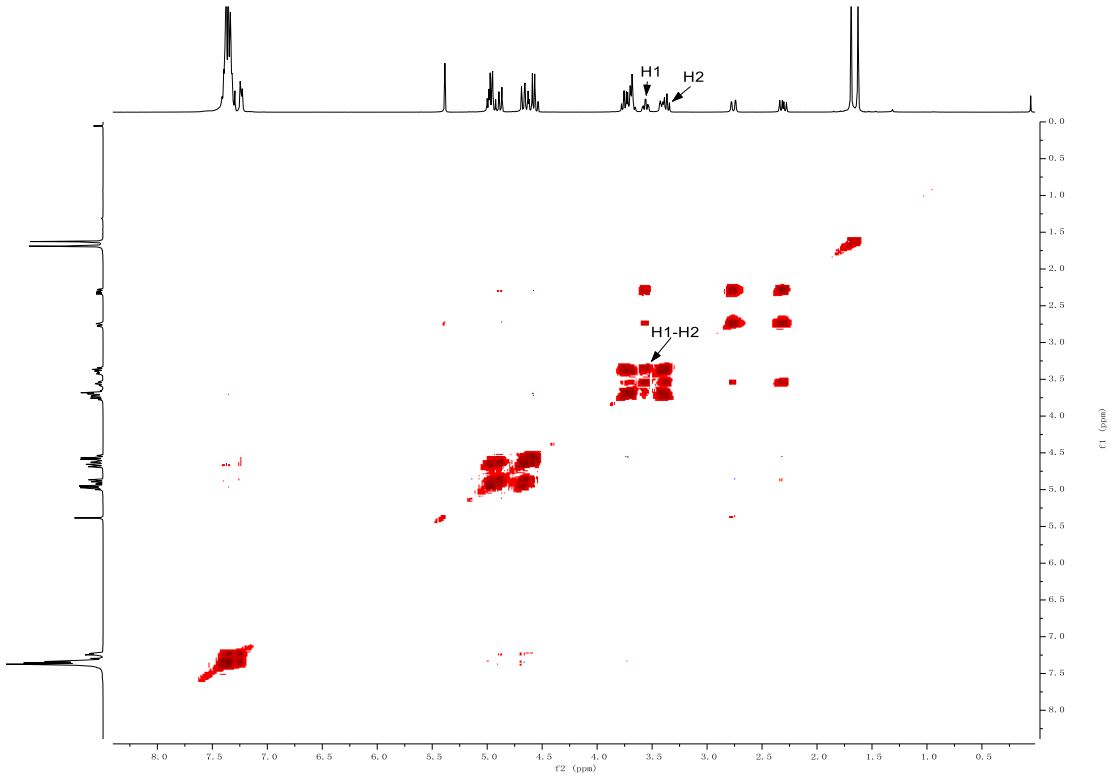
## Compound 4cβ



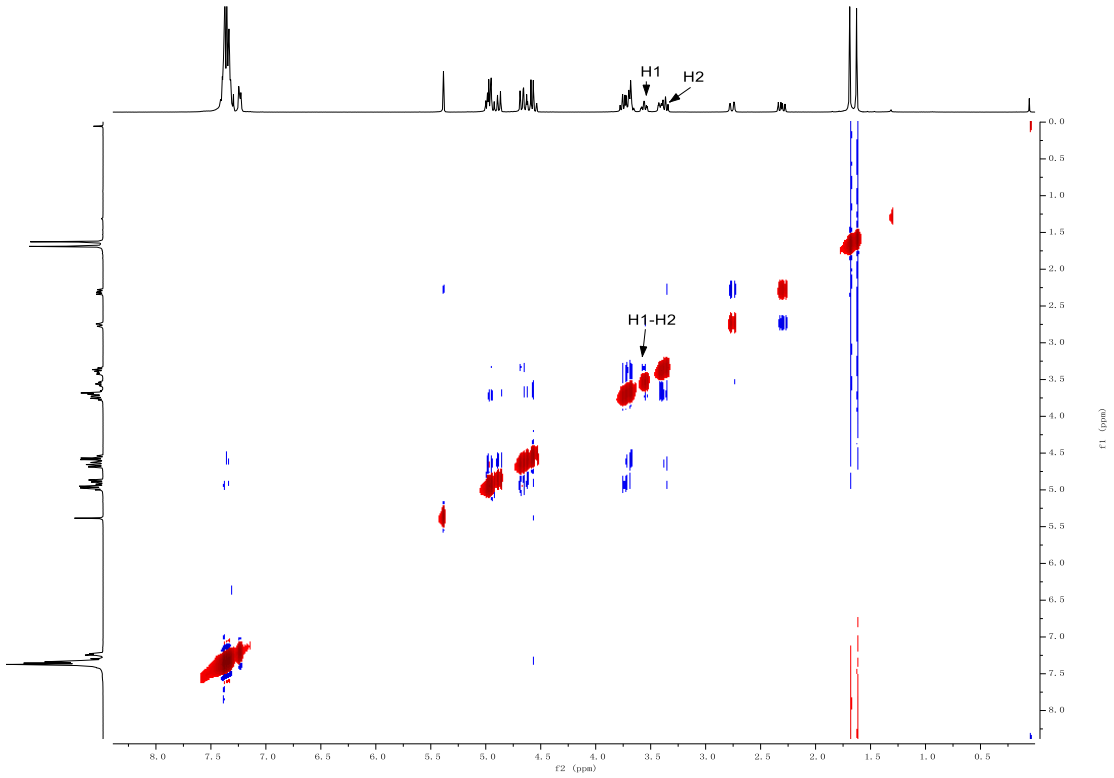

$^{13}$C NMR (100 MHz, $CDCl_3$)



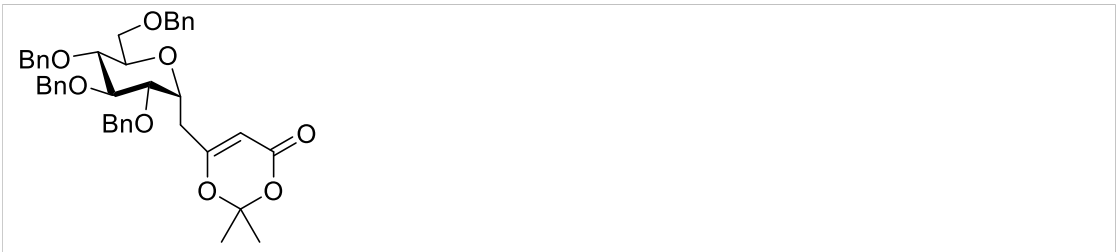
Gcosy NMR (400 MHz, $CDCl_3$)



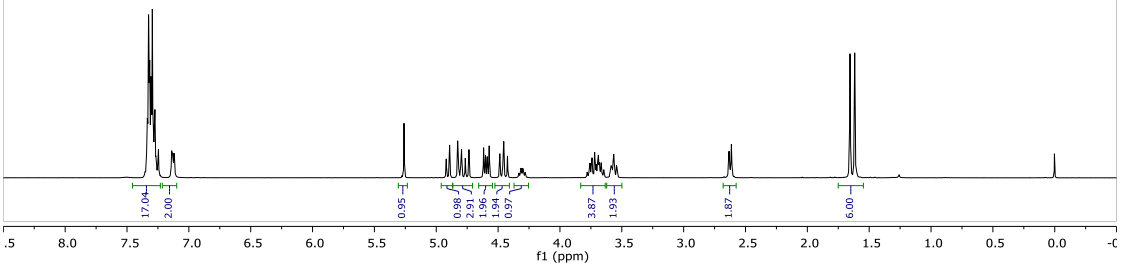

Noesy NMR (400 MHz, $CDCl_3$)



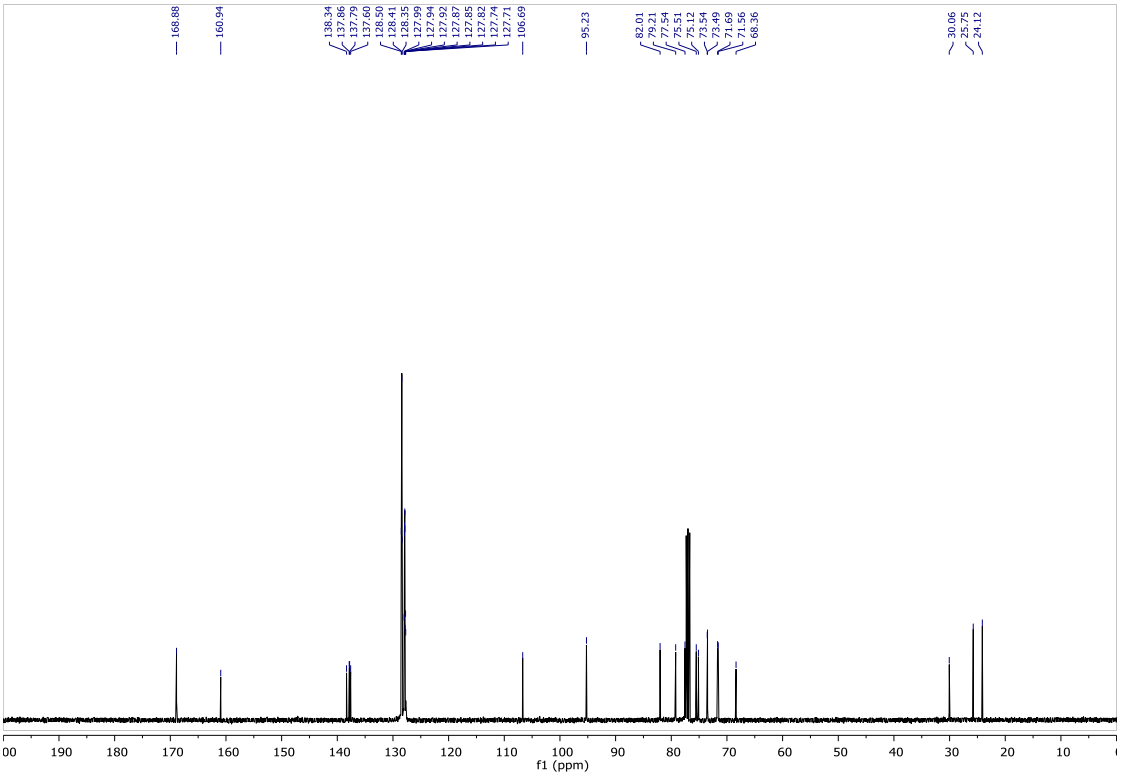
## Compound 4cα



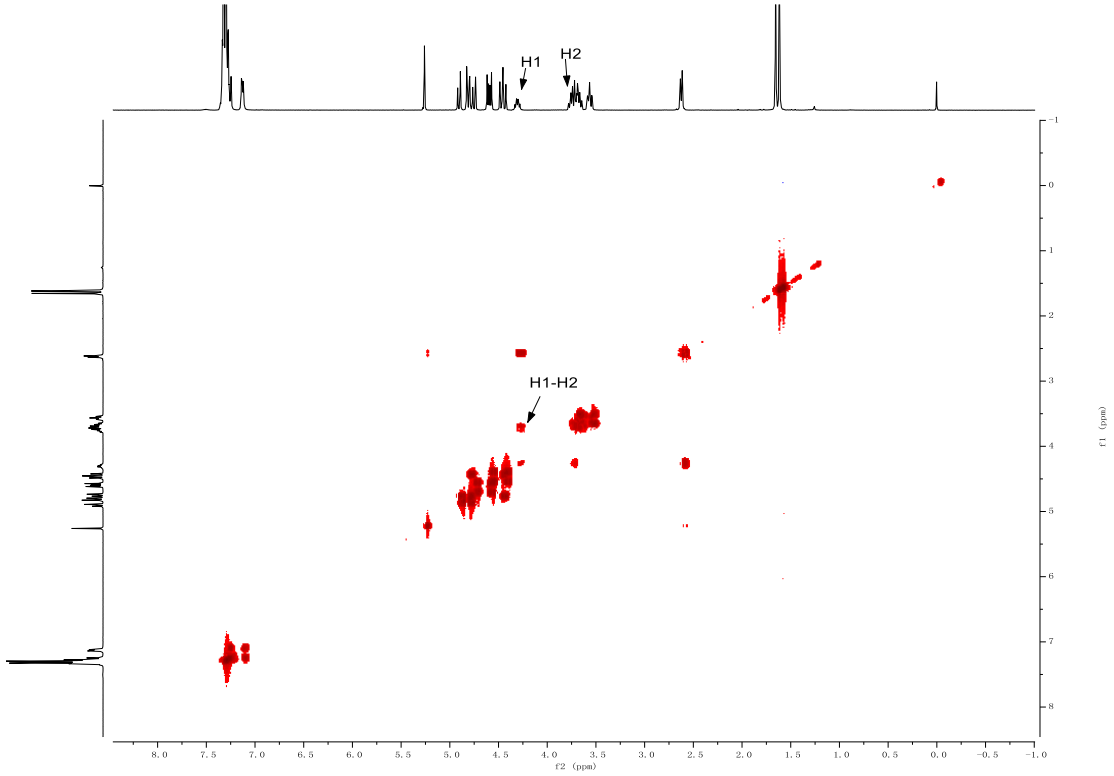

$^{1}$H NMR (400 MHz, $CDCl_3$)



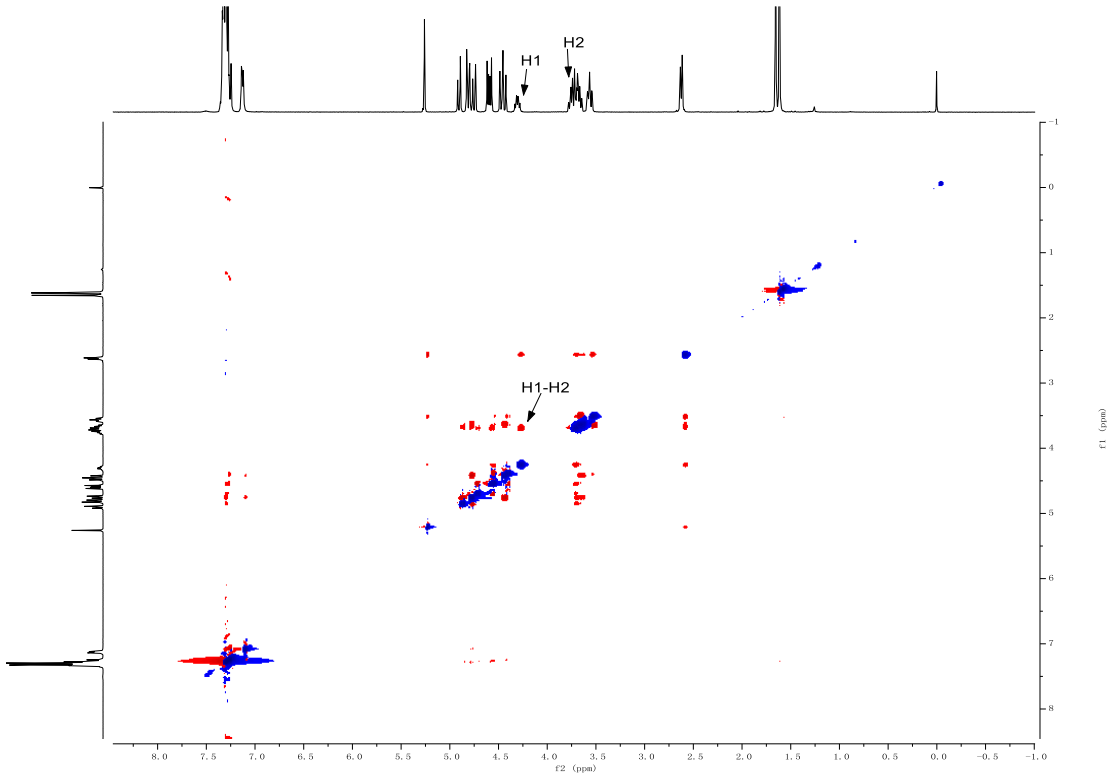

$^{13}$C NMR (100 MHz, $CDCl_3$)



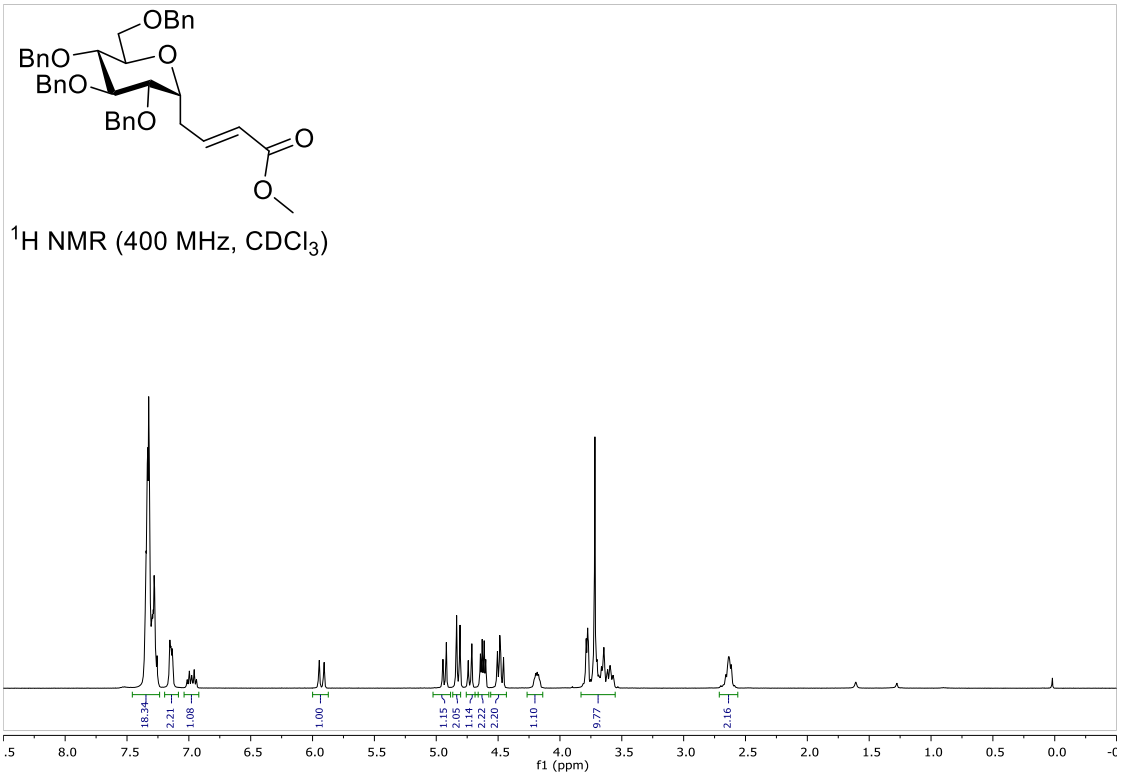
Gcosy NMR (400 MHz, $CDCl_3$)



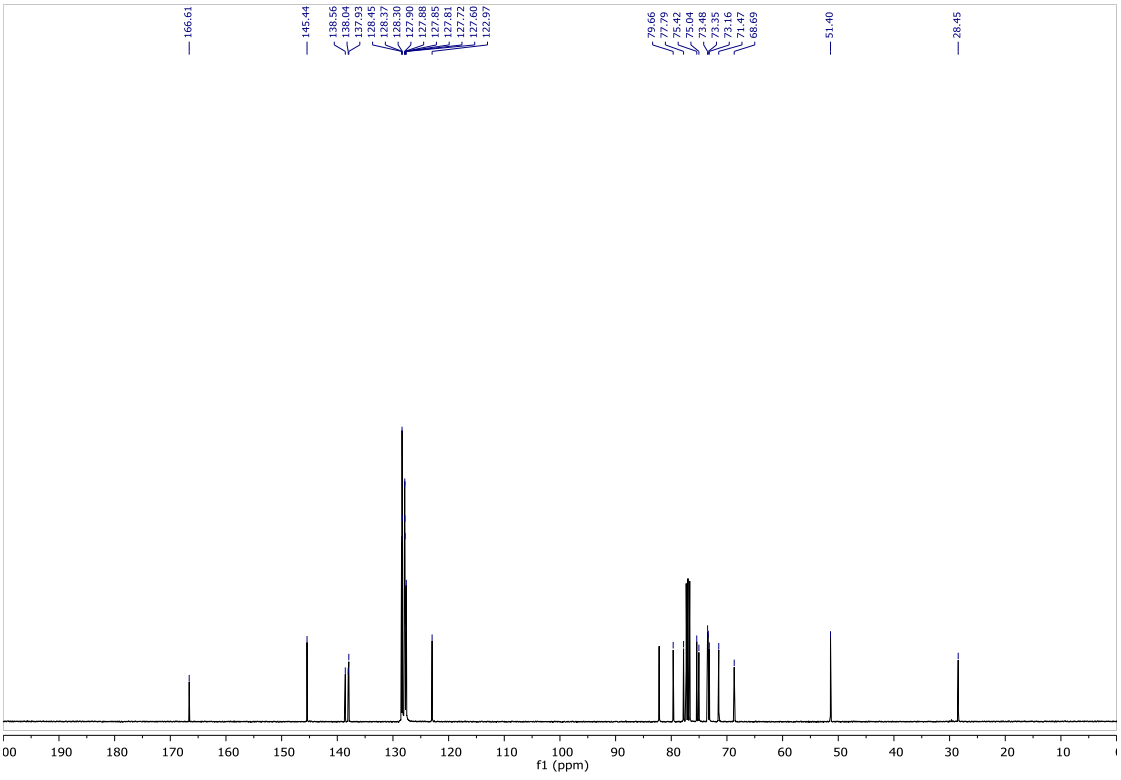

Noesy NMR (400 MHz, $CDCl_3$)



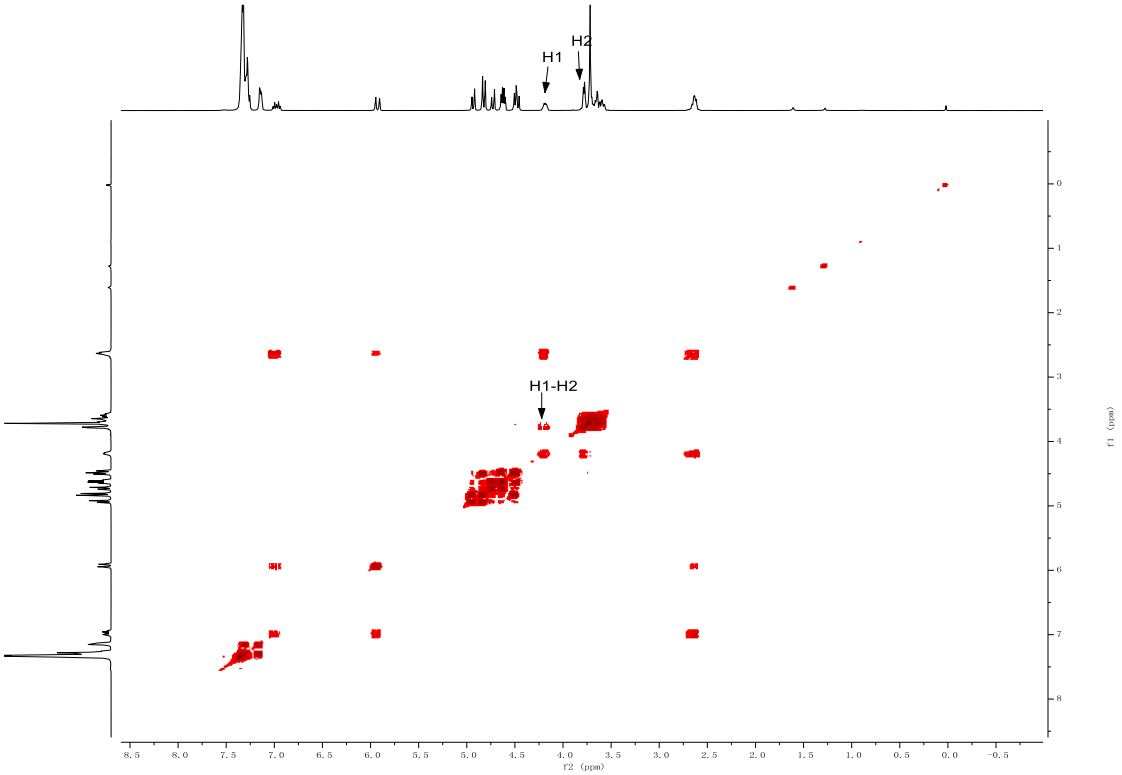
## Compound 4dα



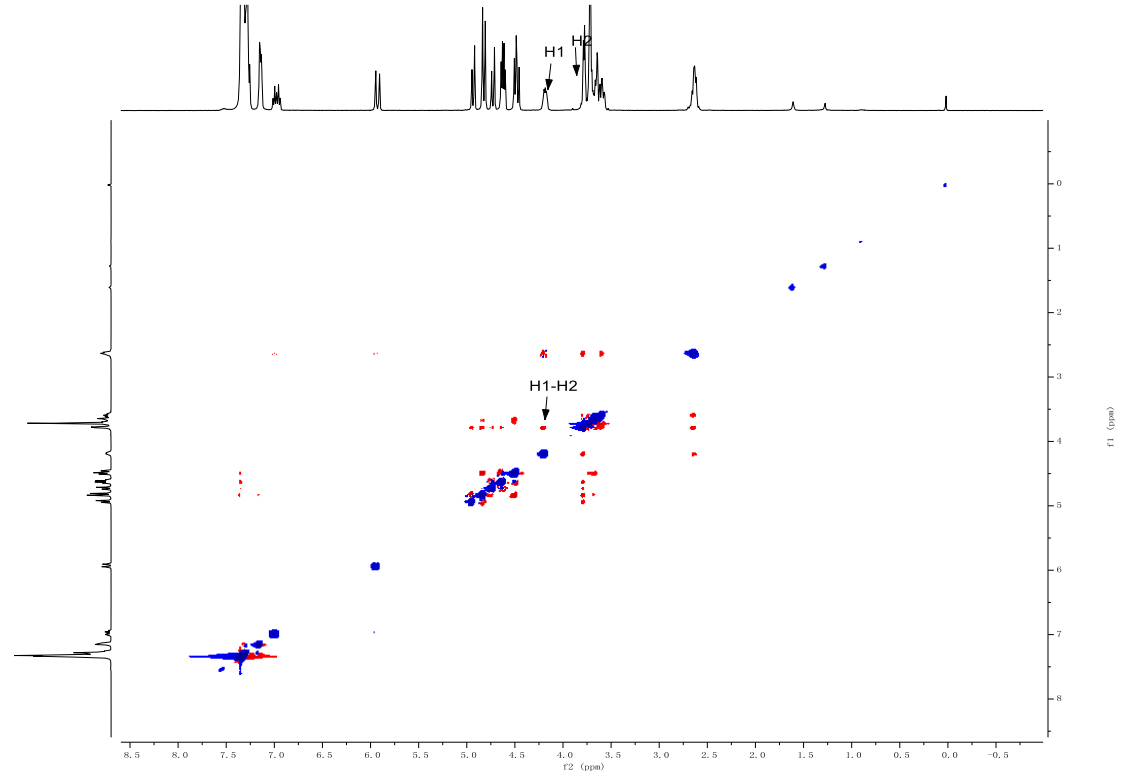

$^{13}C$ NMR (100 MHz, $CDCl_3$)



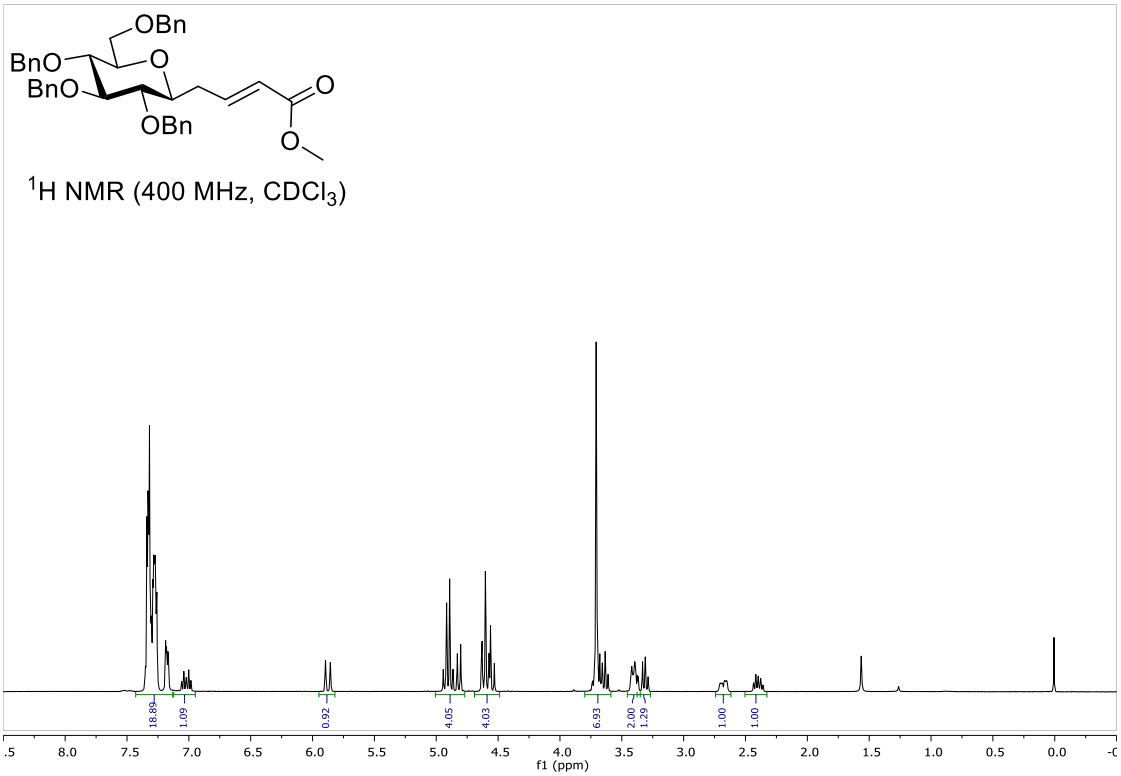
Gcosy NMR (400 MHz, $CDCl_3$)



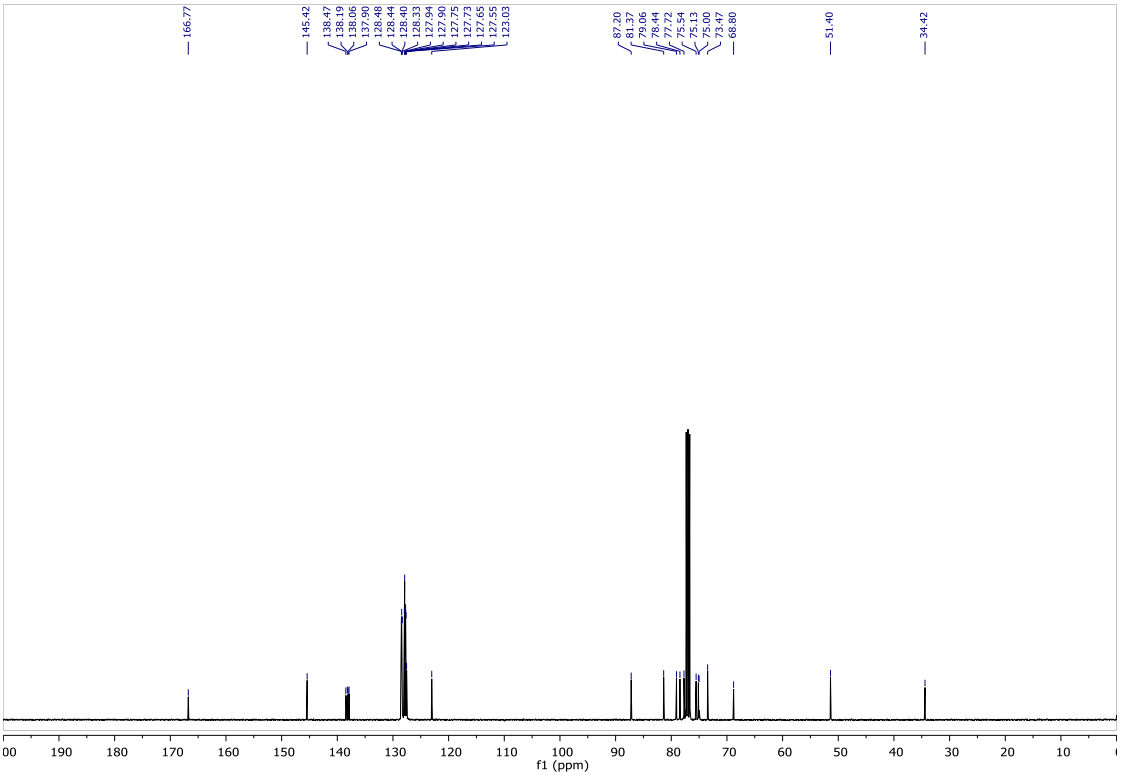

Neosy NMR (400 MHz, $CDCl_3$)



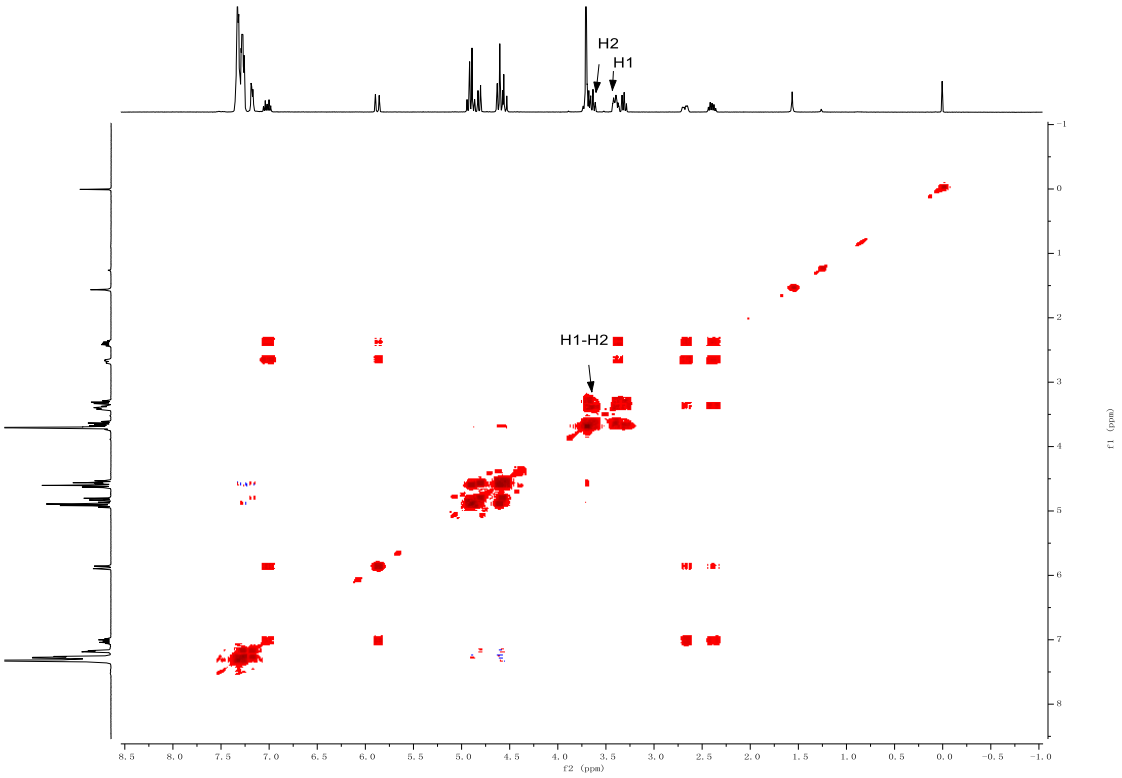
**Compound 4dβ**



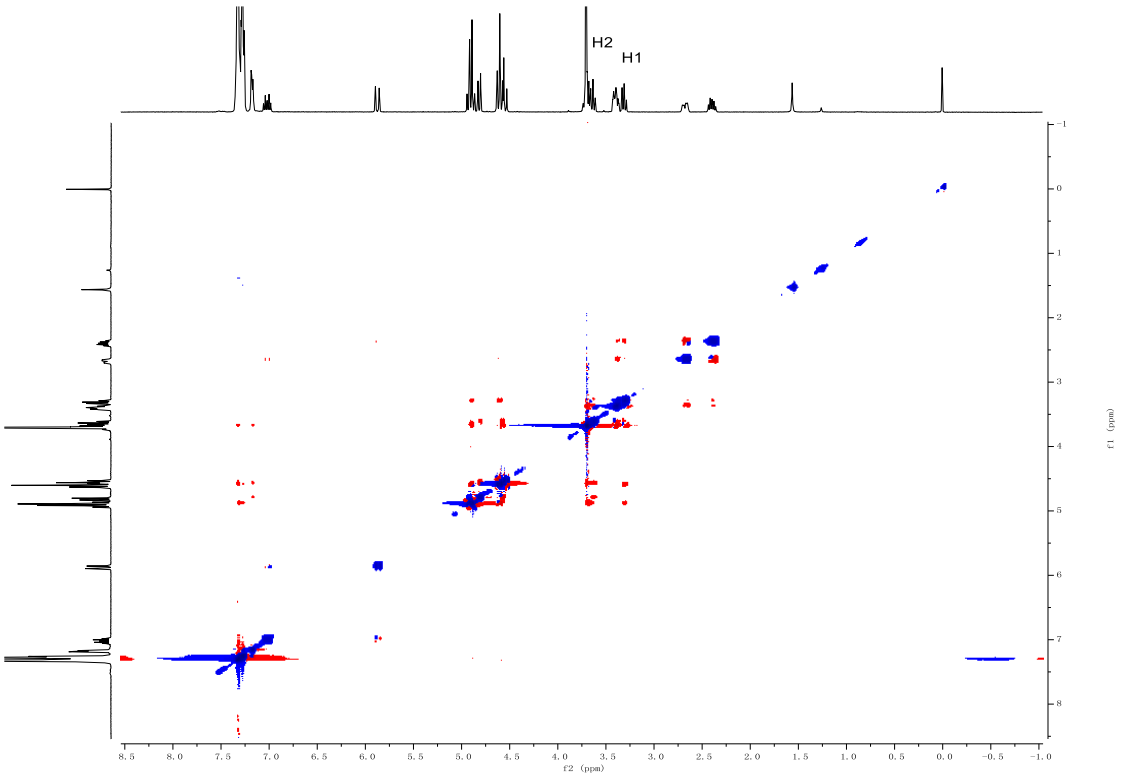

$^{13}$C NMR (100 MHz, CDCl$_3$)



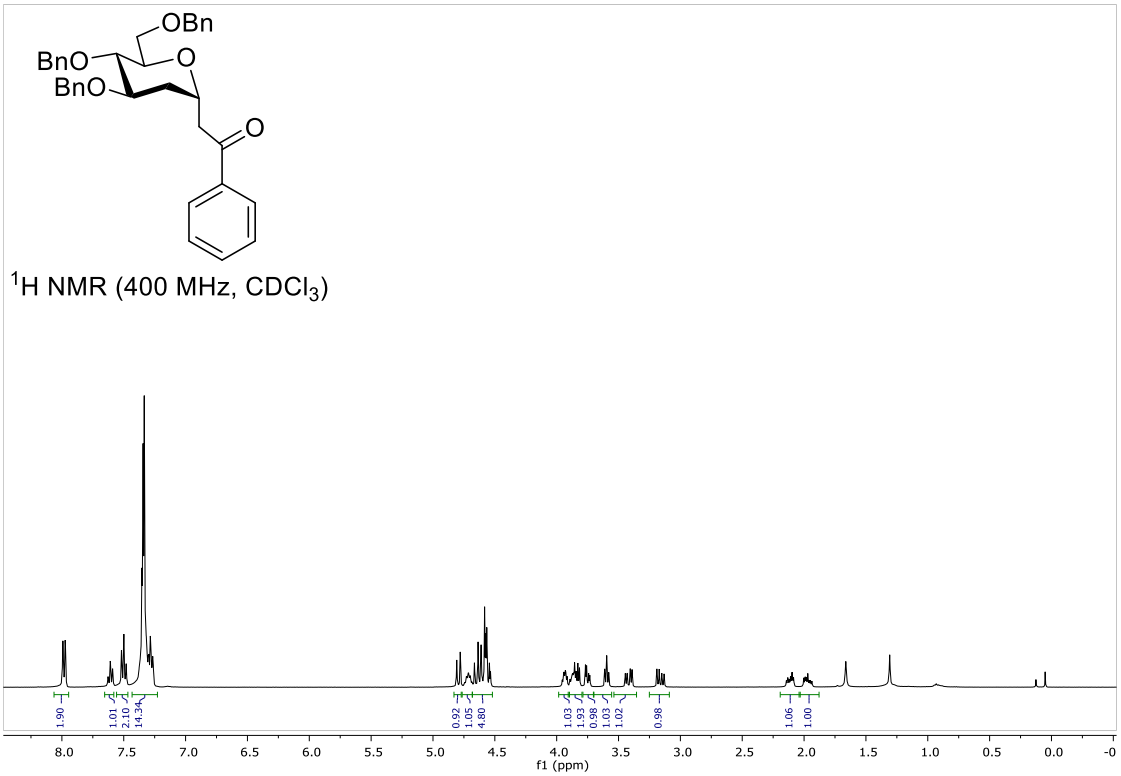
Gcosy NMR (400 MHz, $CDCl_3$)



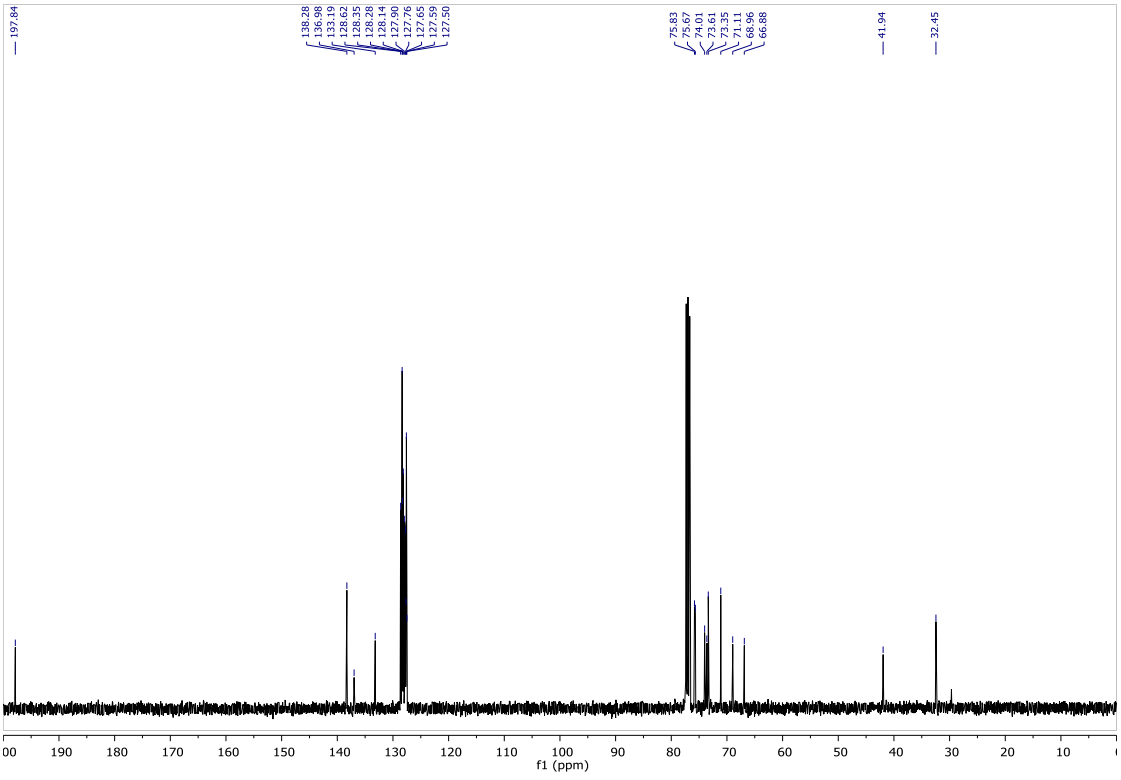

Neosy NMR (400 MHz, $CDCl_3$)



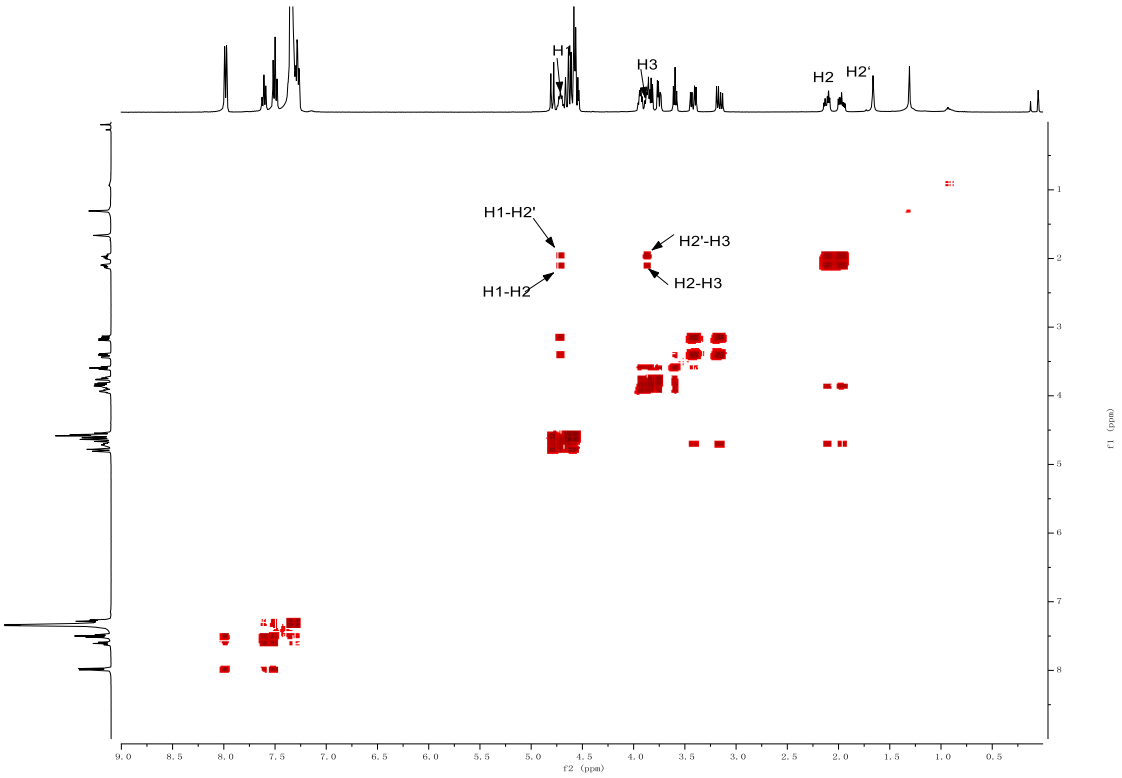
## Compound 4eα



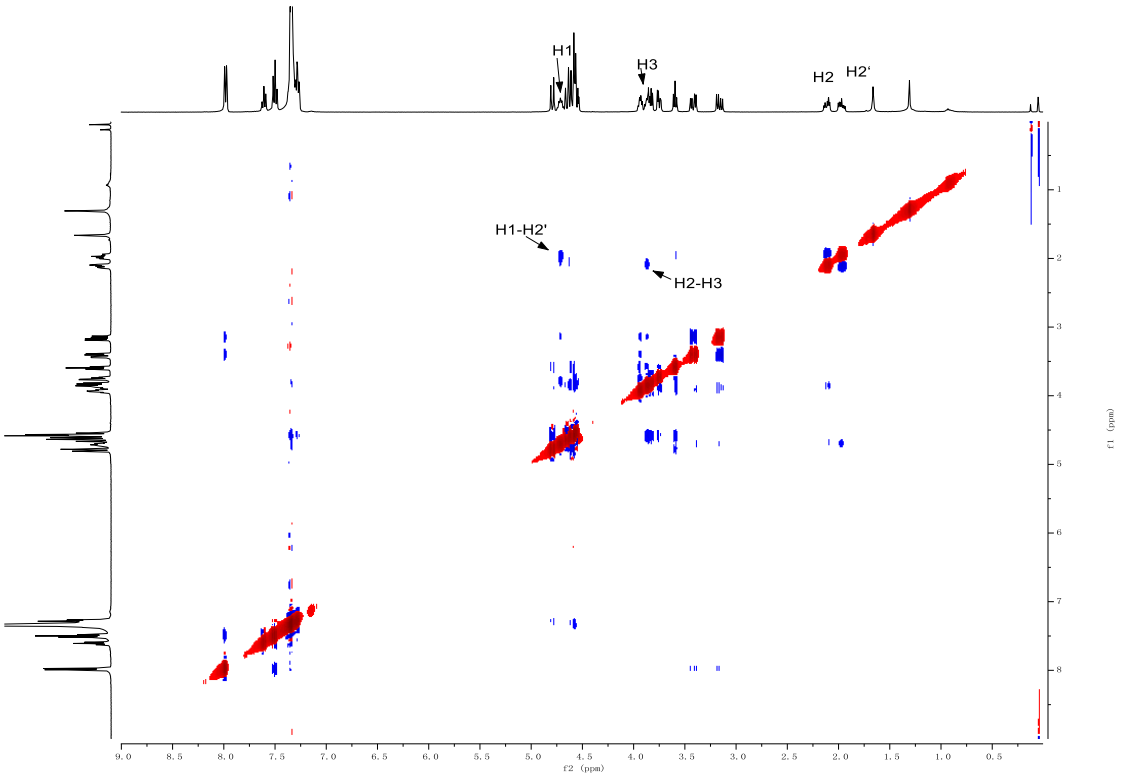

$^{13}$C NMR (100 MHz, $CDCl_3$)



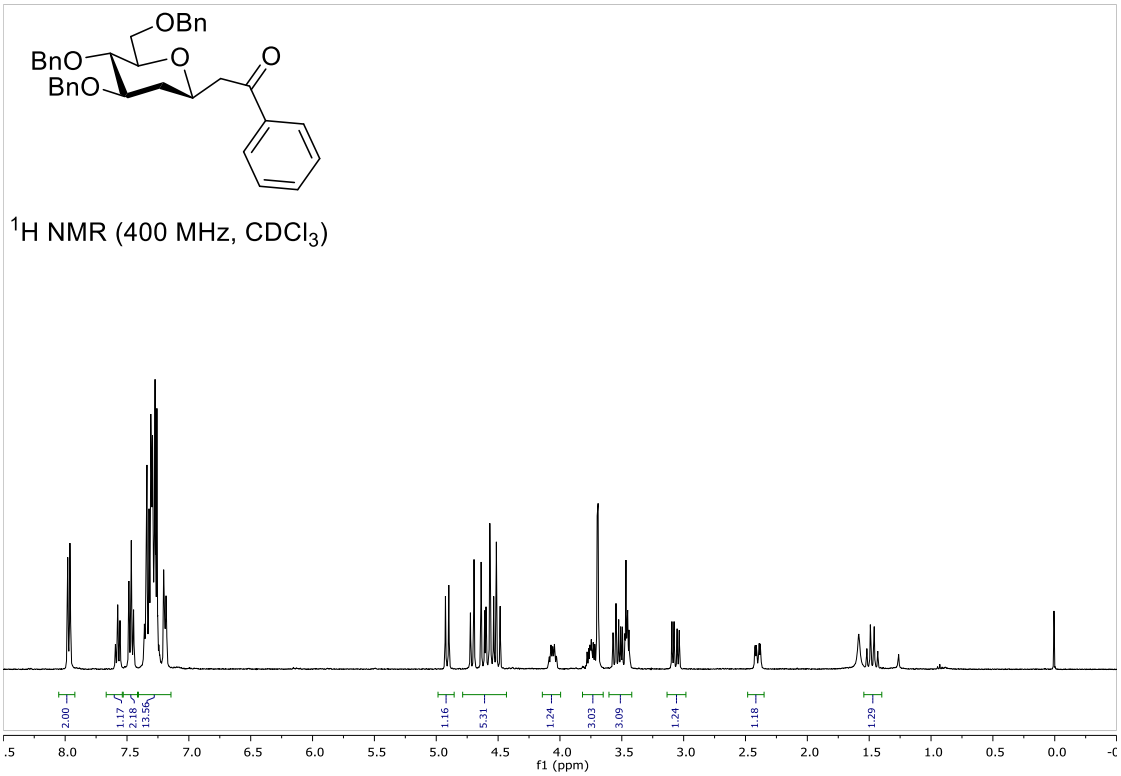
Gcosy NMR (400 MHz, $CDCl_3$)



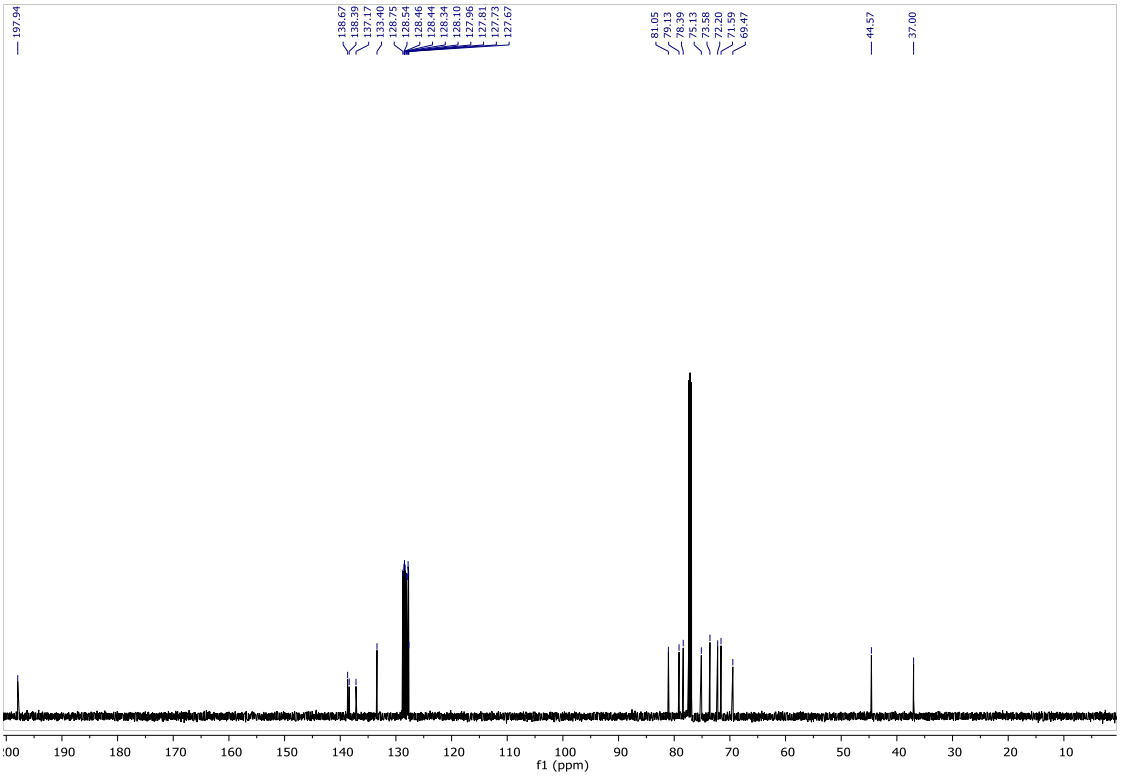

Neosy NMR (400 MHz, $CDCl_3$)



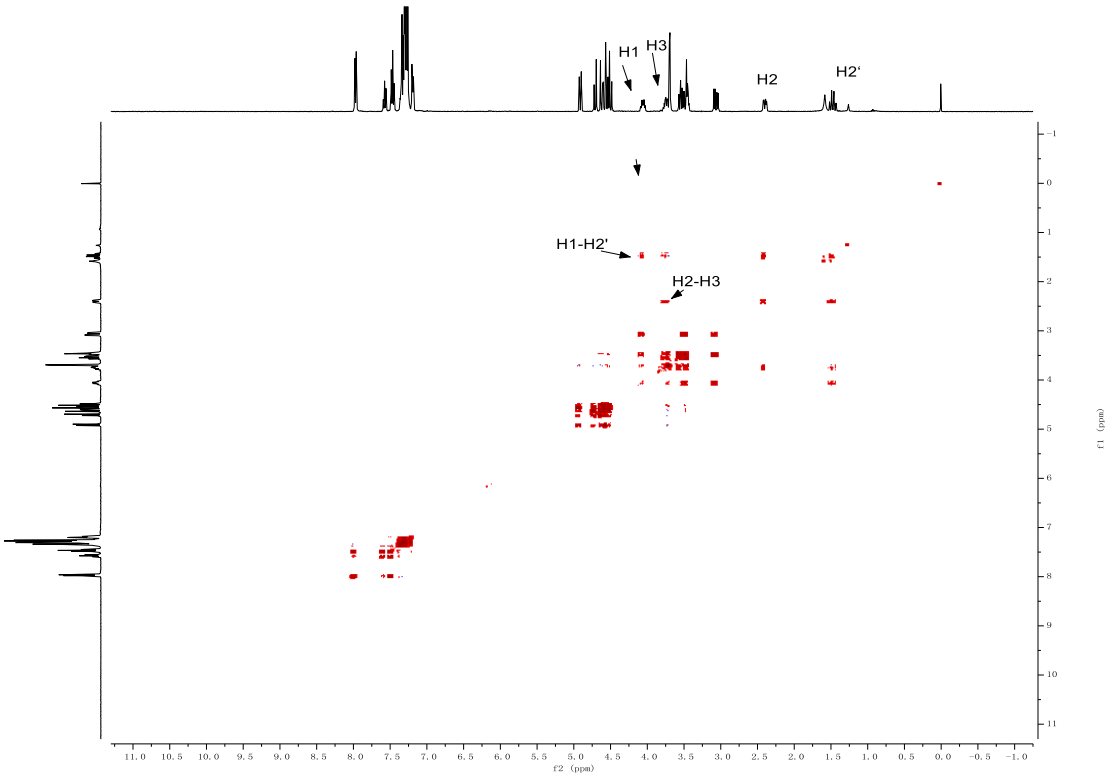
## Compound 4eβ



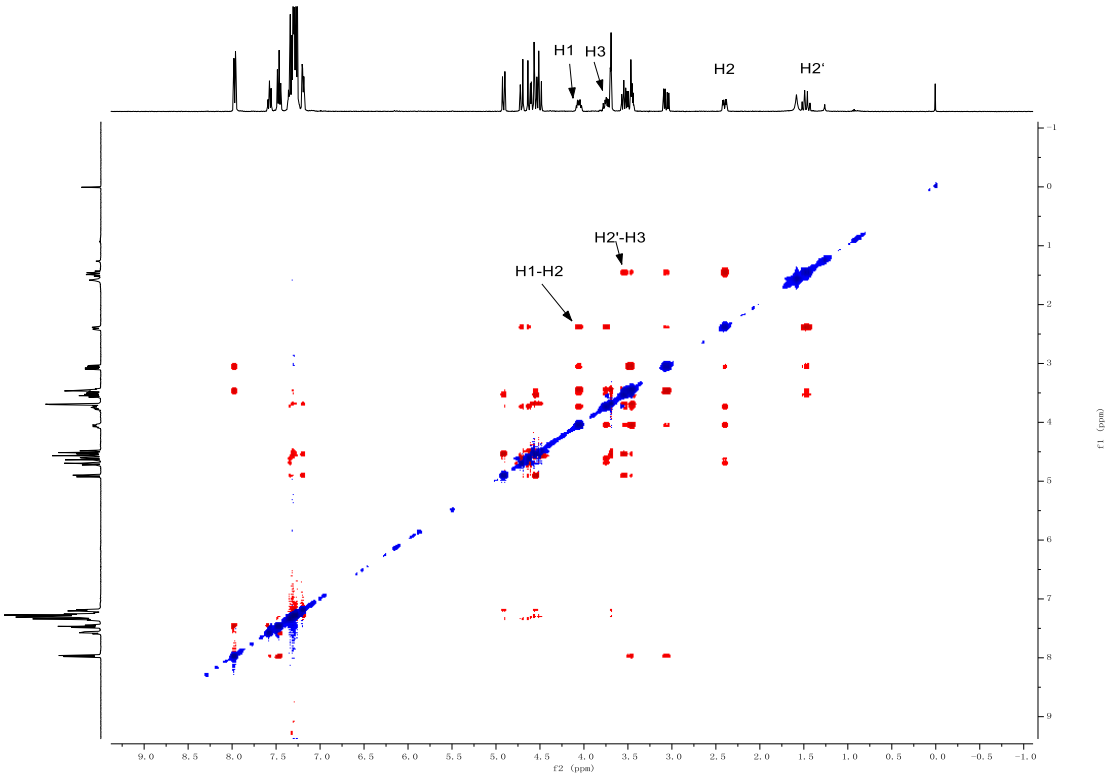

$^{13}$C NMR (125 MHz, $CDCl_3$)



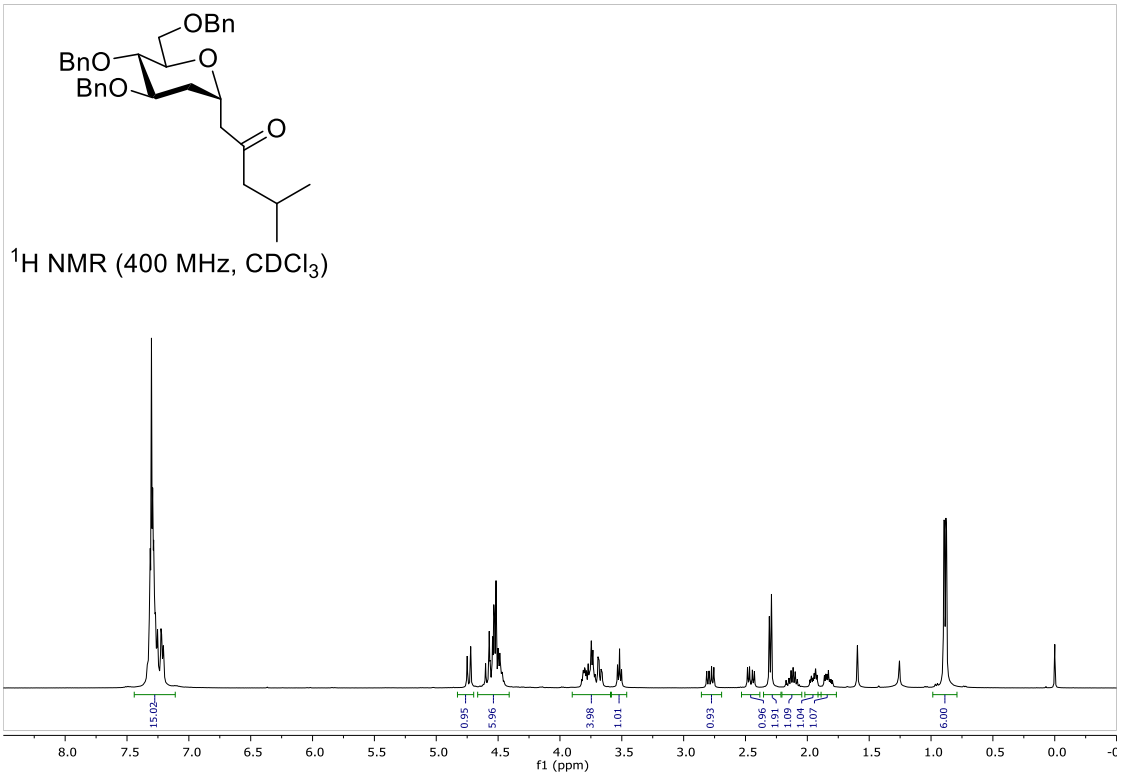
Gcosy NMR (400 MHz, $CDCl_3$)



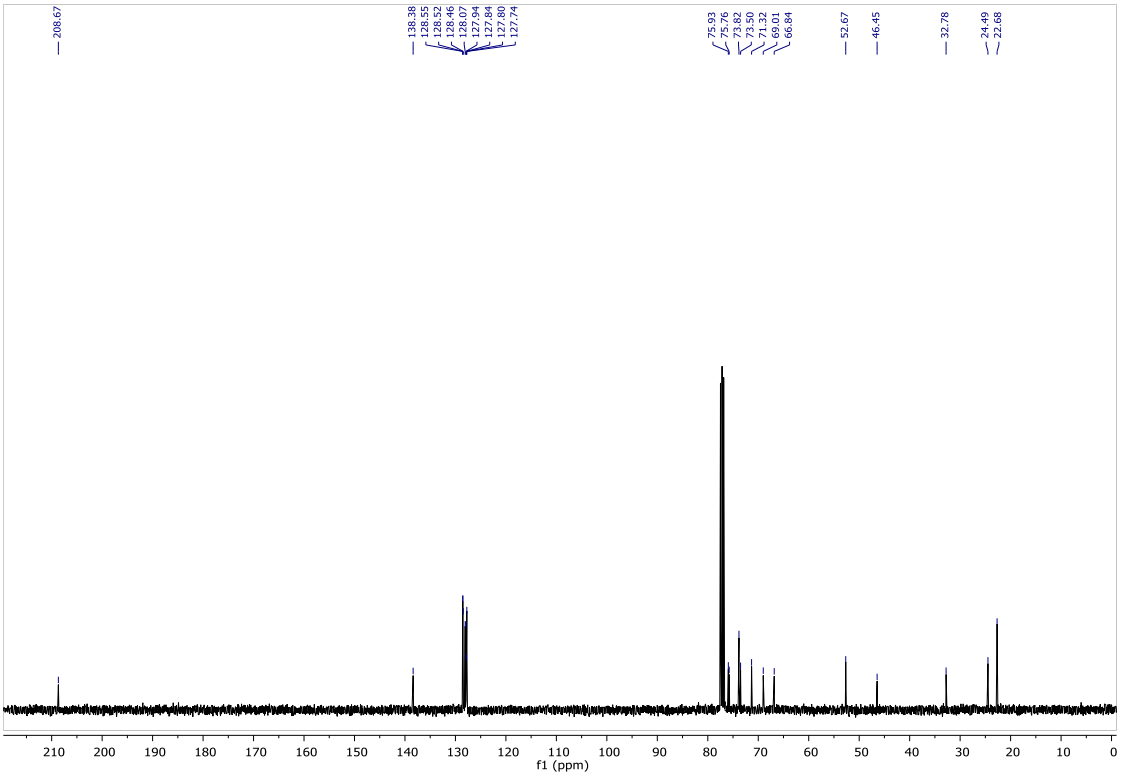

Noesy NMR (400 MHz, $CDCl_3$)



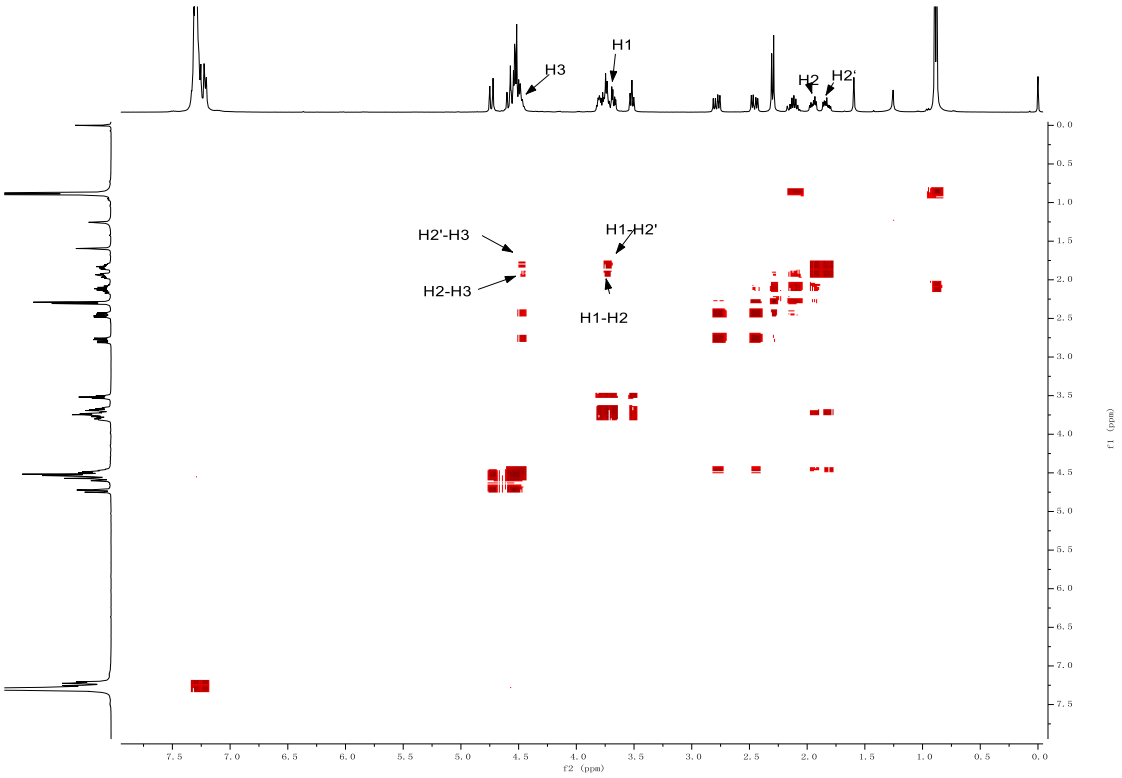
## Compound 4fα



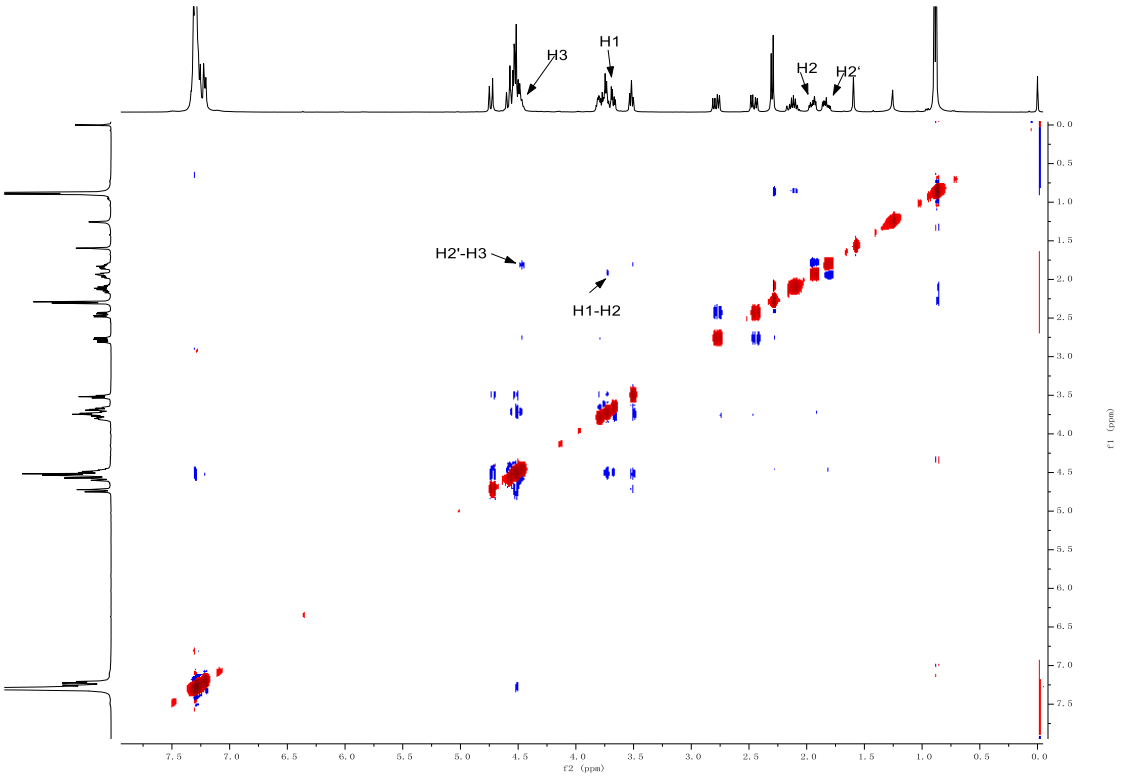

$^{13}$C NMR (100 MHz, $CDCl_3$)



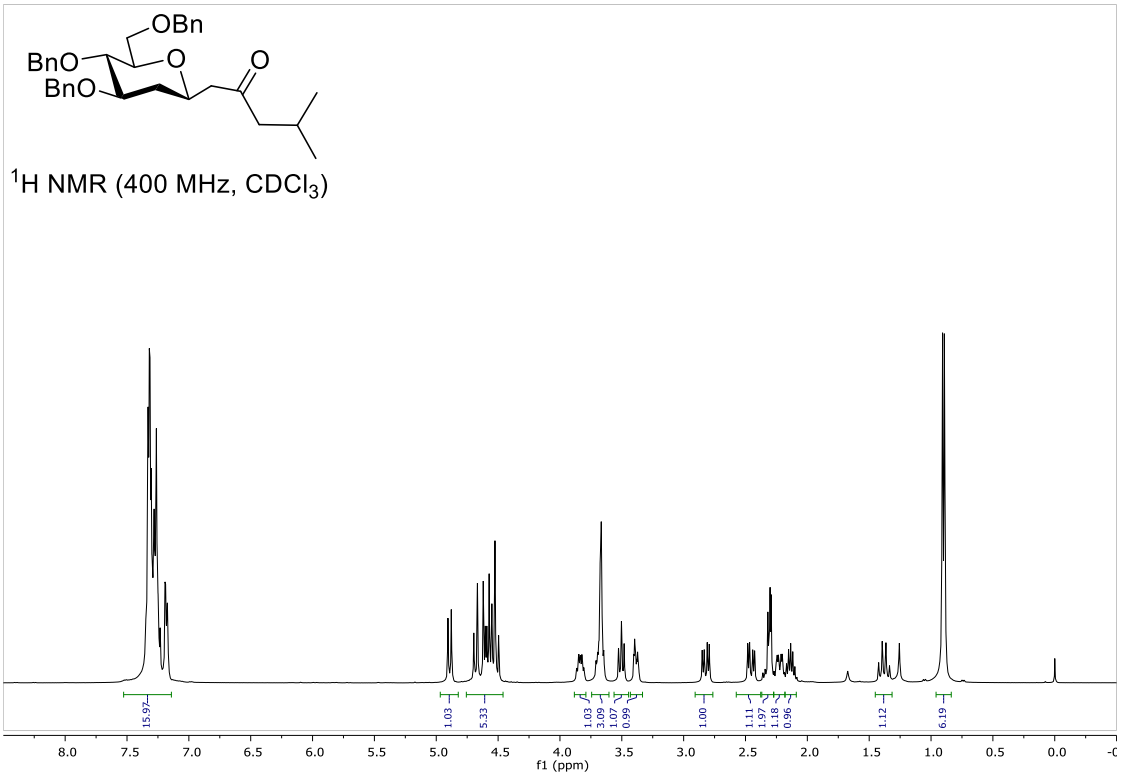
Gcosy NMR (400 MHz, $CDCl_3$)



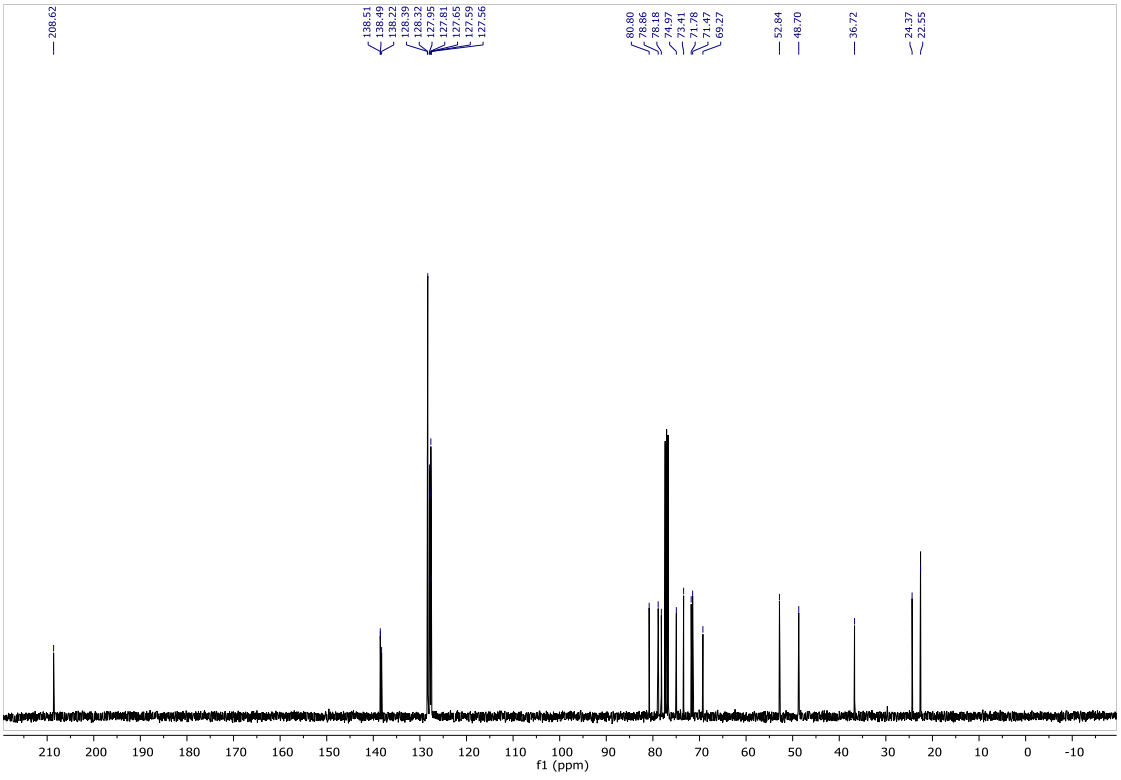

Noesy NMR (400 MHz, $CDCl_3$)



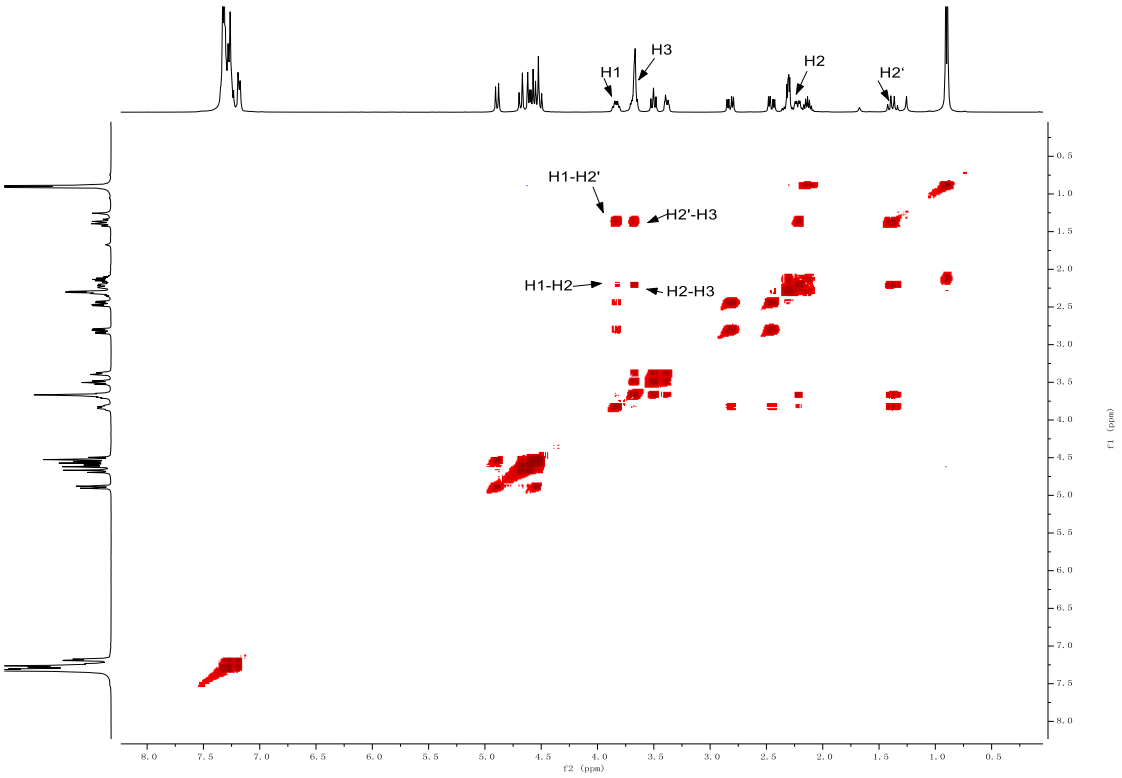
## Compound 4fβ



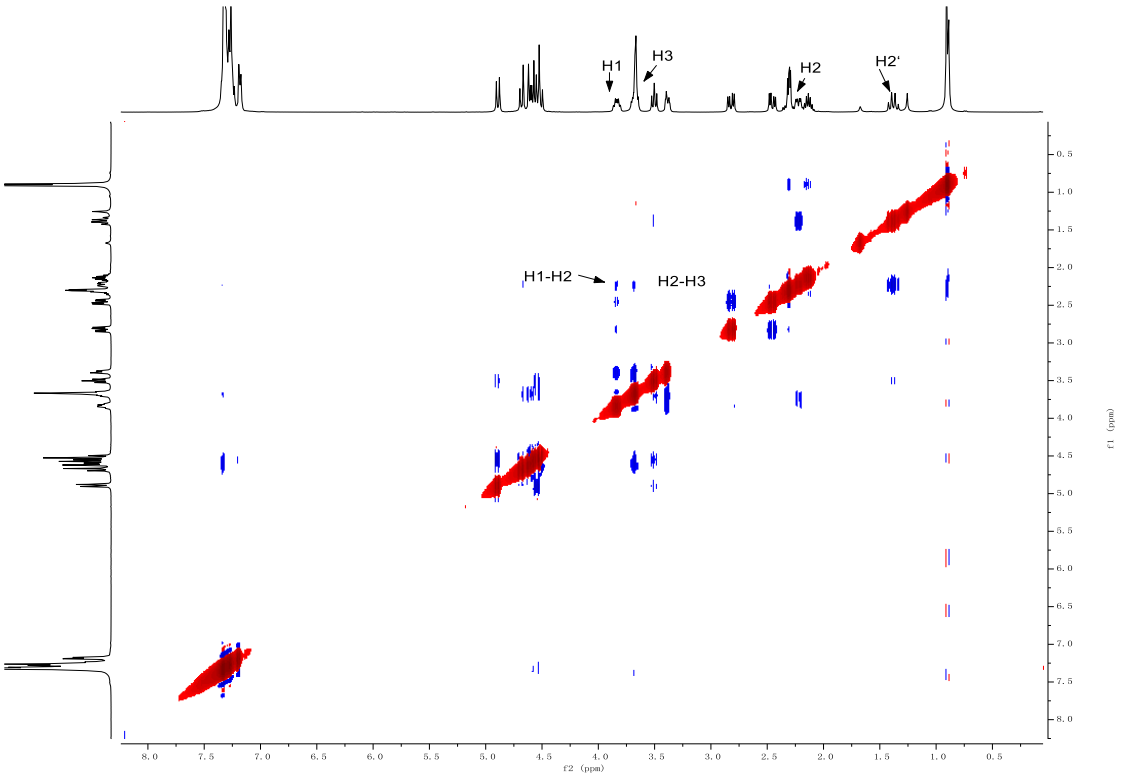

$^{13}C$ NMR (100 MHz, $CDCl_3$)



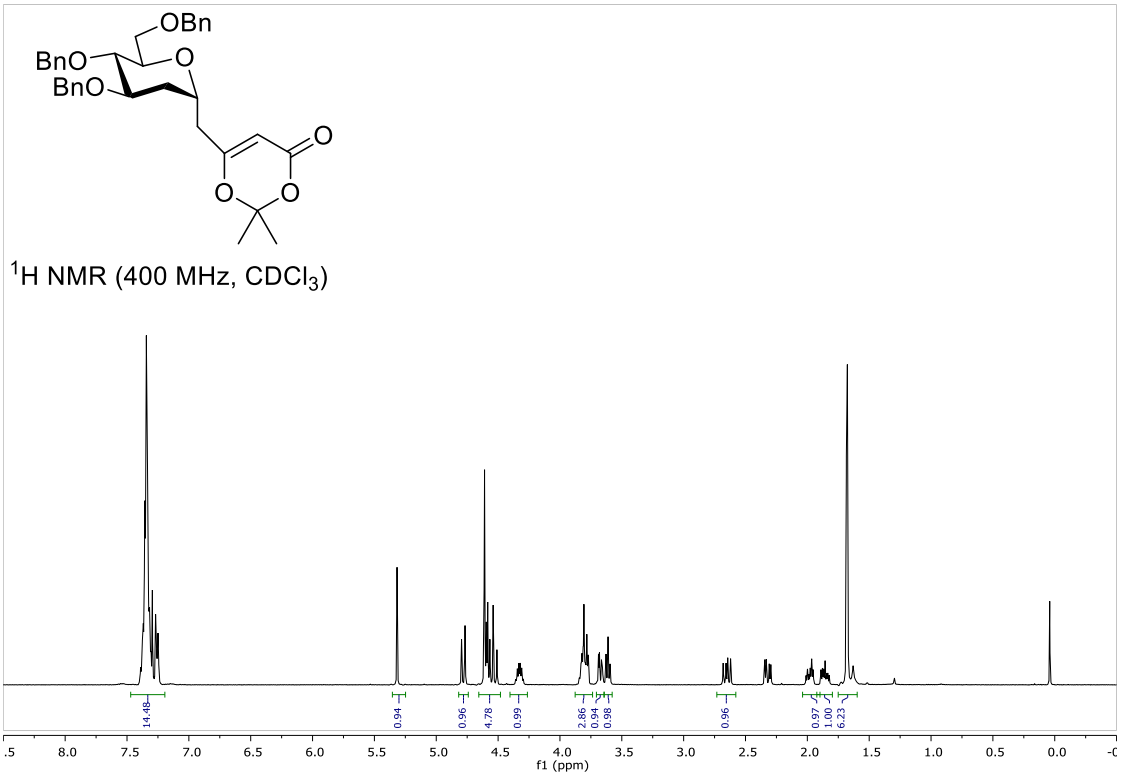
Gcosy NMR (400 MHz, $CDCl_3$)



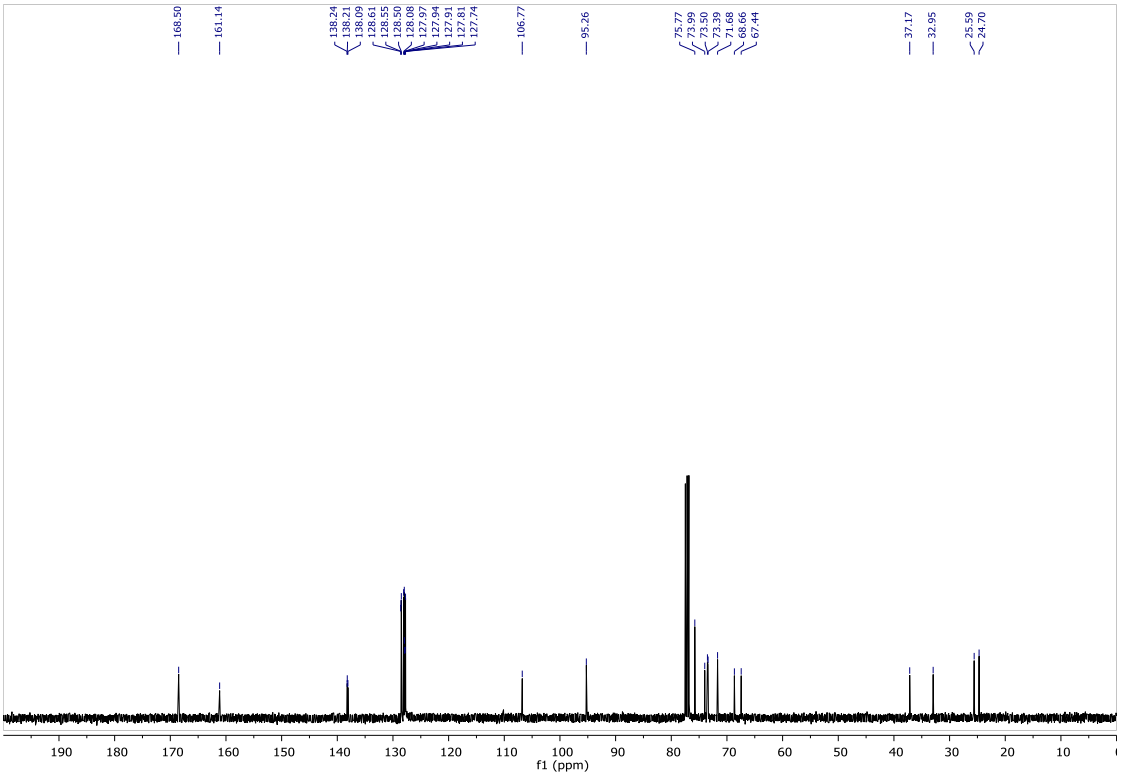

Noesy NMR (400 MHz, $CDCl_3$)



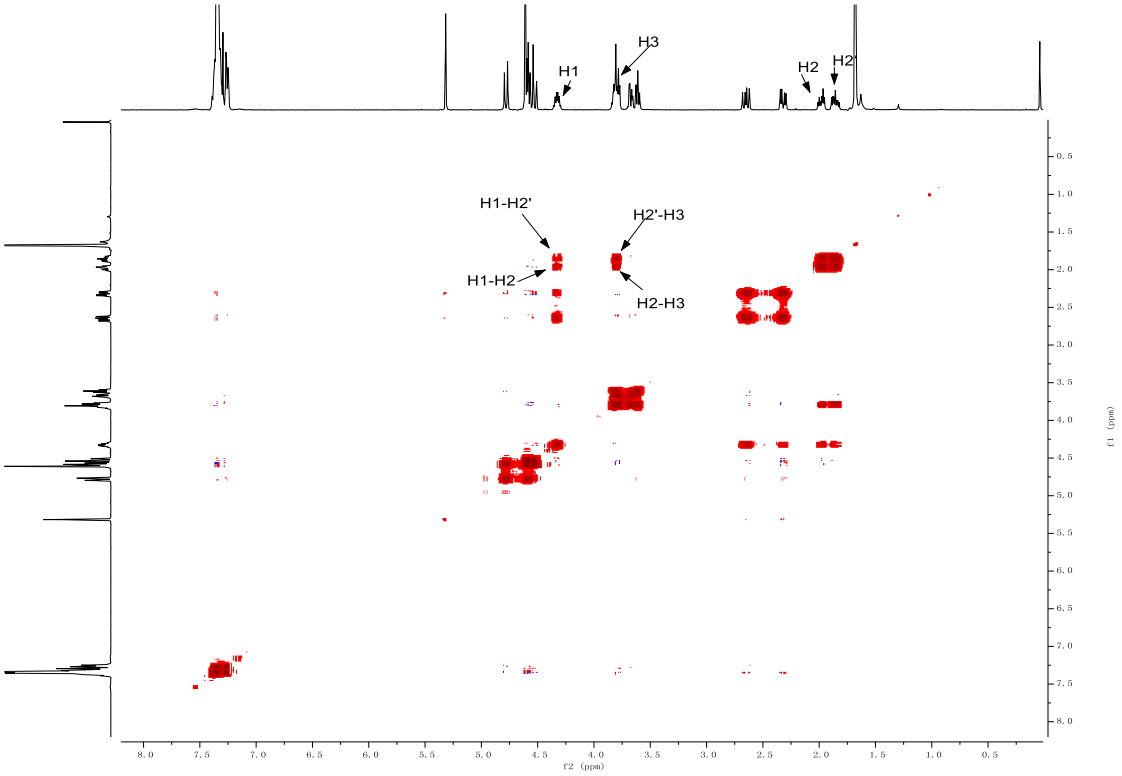
## Compound 4gα



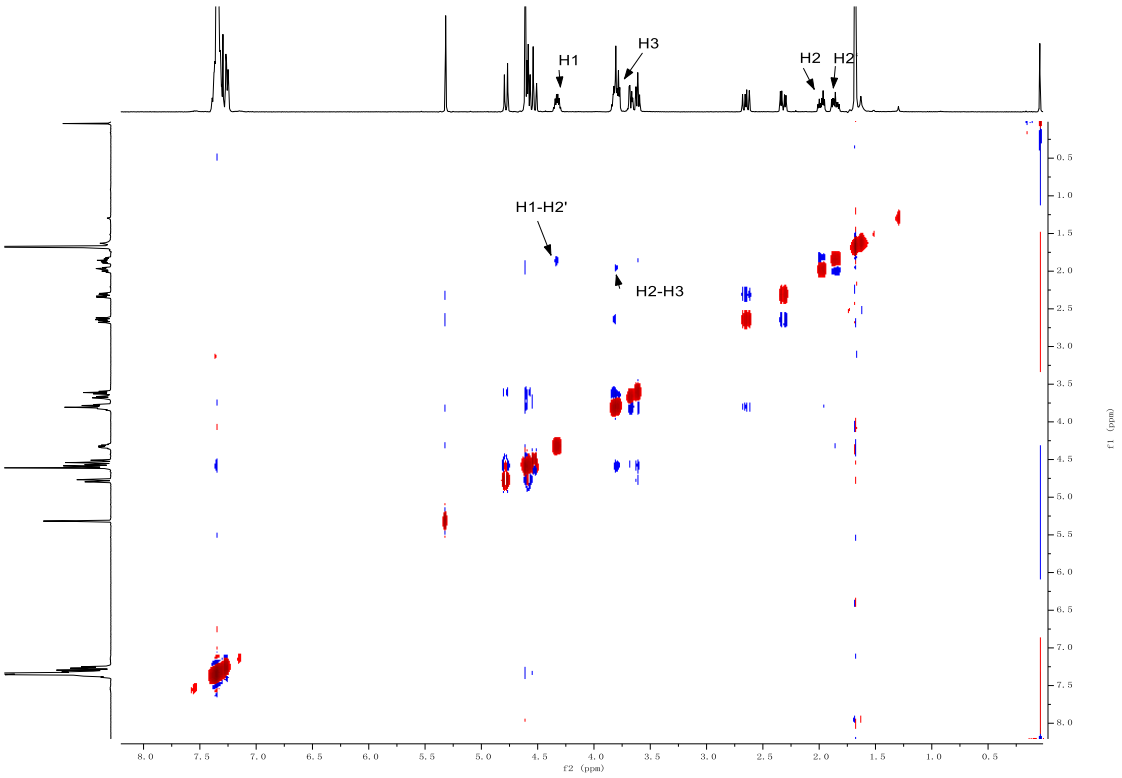

$^{13}$C NMR (100 MHz, $CDCl_3$)



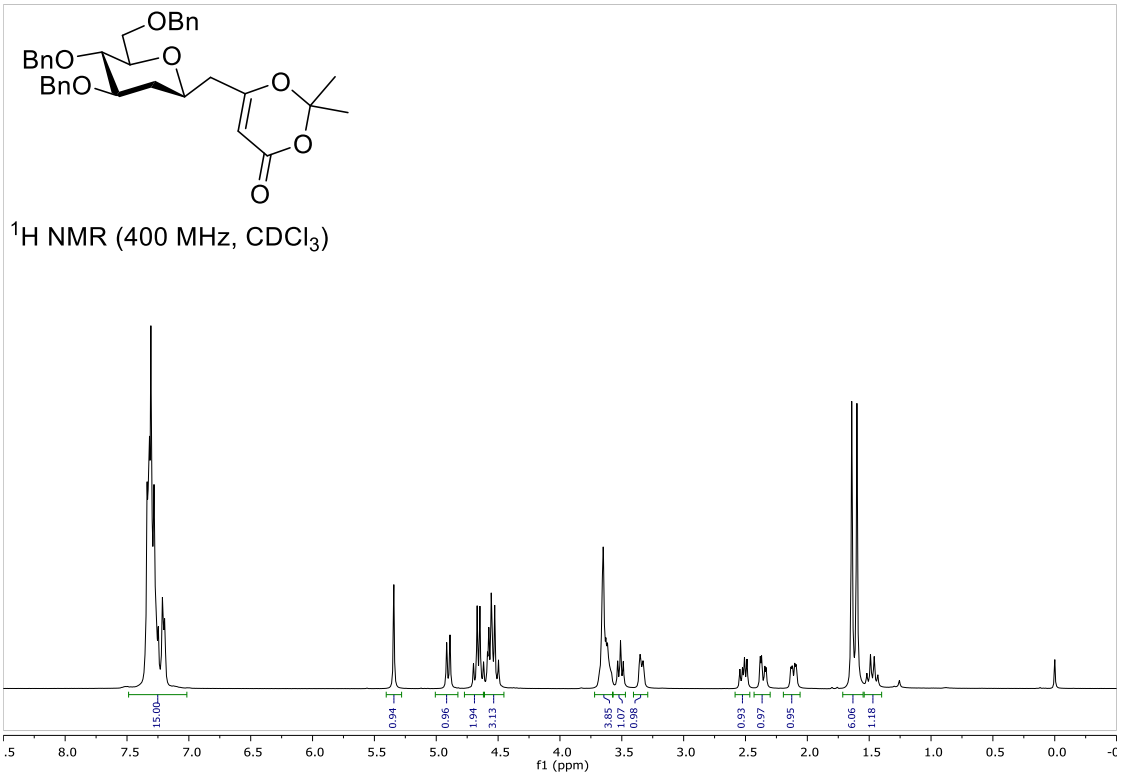
Gcosy NMR (400 MHz, $CDCl_3$)



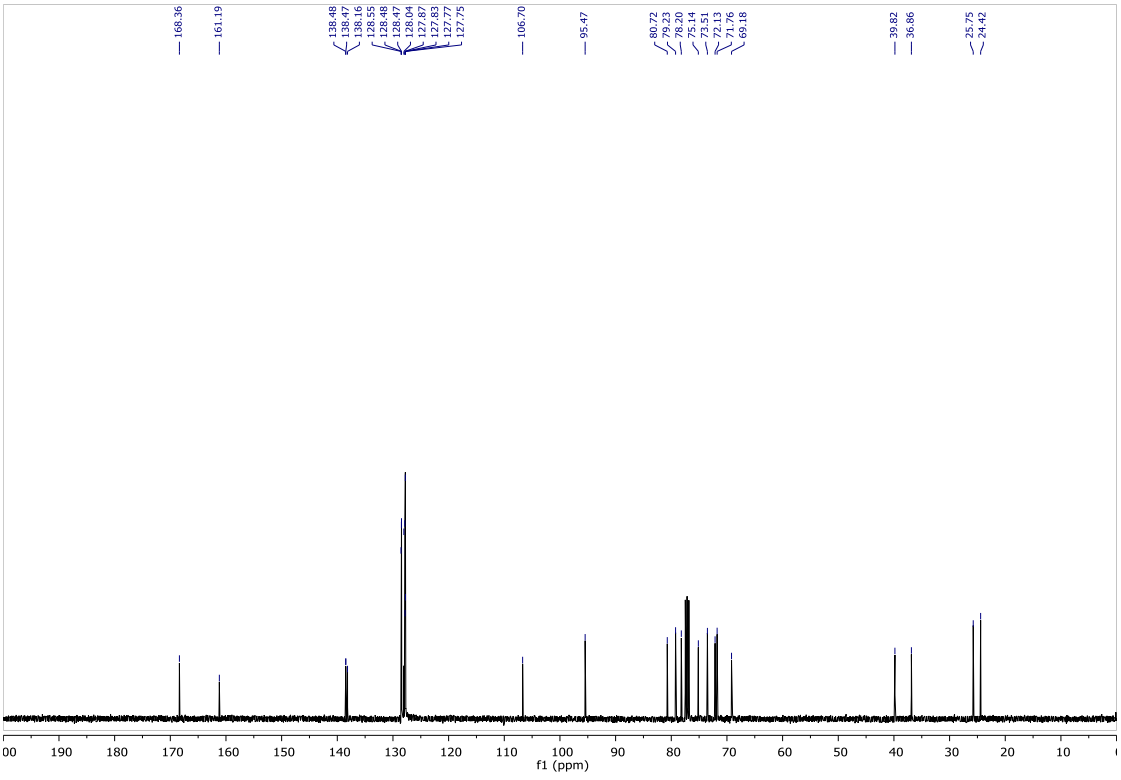

Noesy NMR (400 MHz, $CDCl_3$)



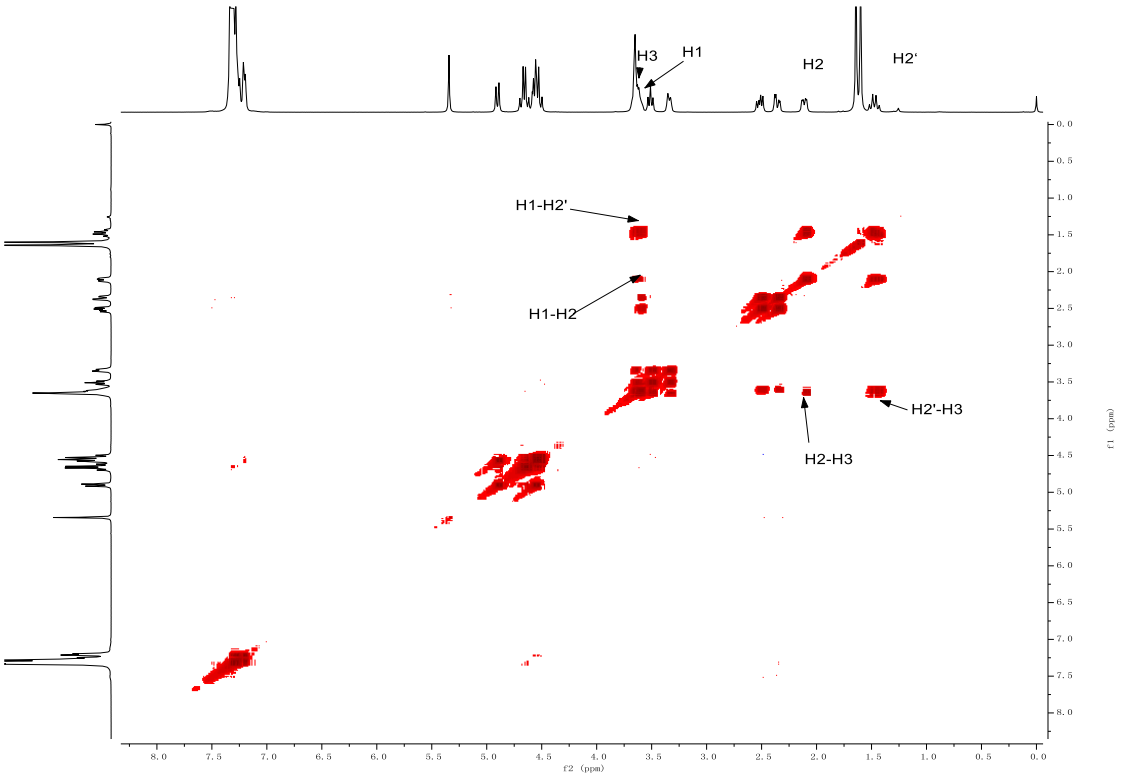
## Compound 4gβ



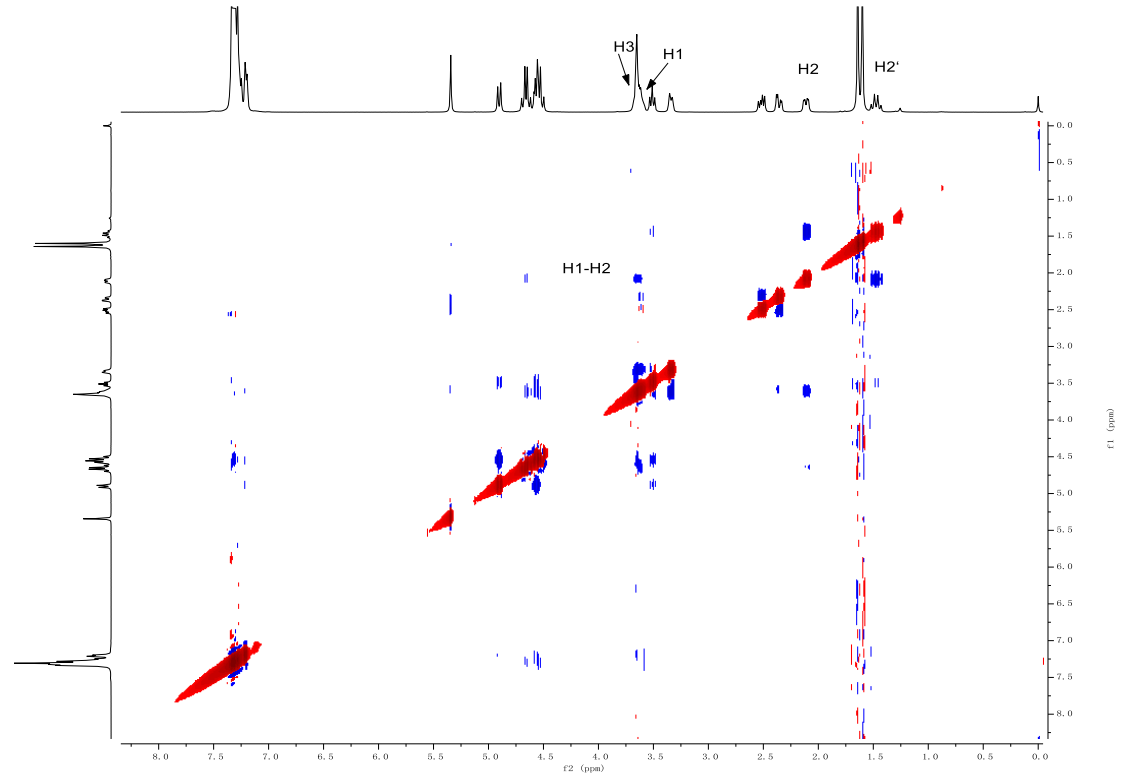

$^{13}$C NMR (100 MHz, $CDCl_3$)



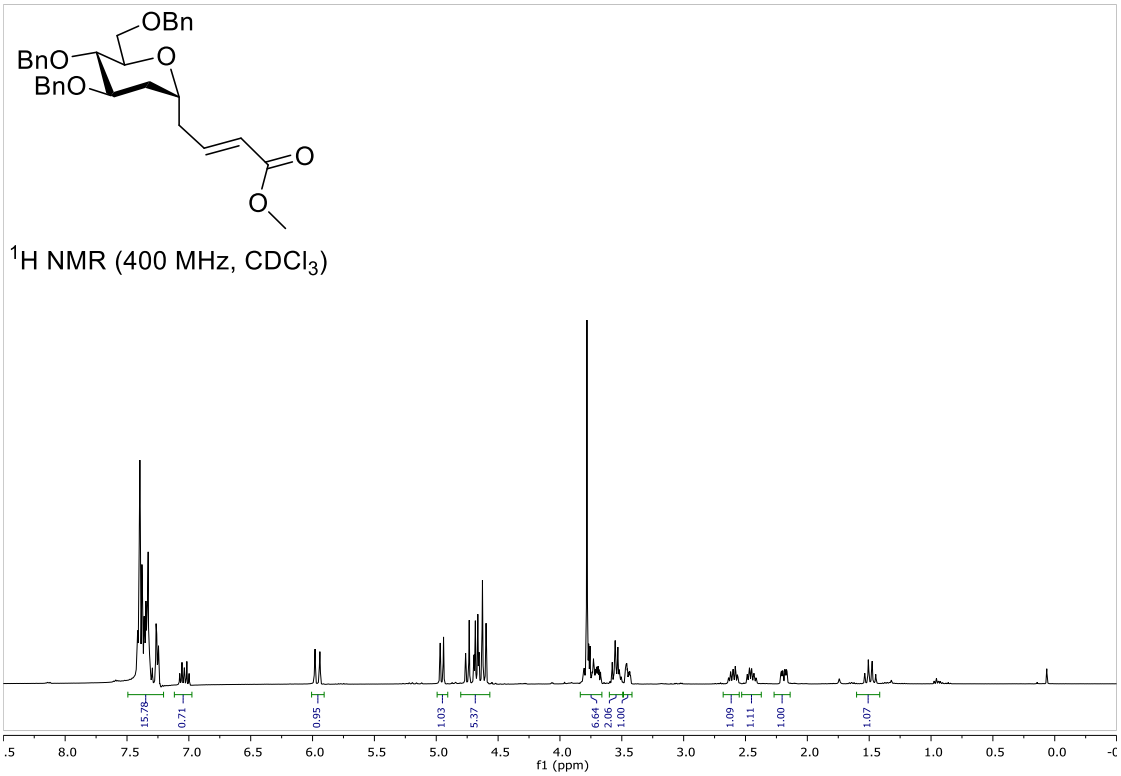
Gcosy NMR (400 MHz, $CDCl_3$)



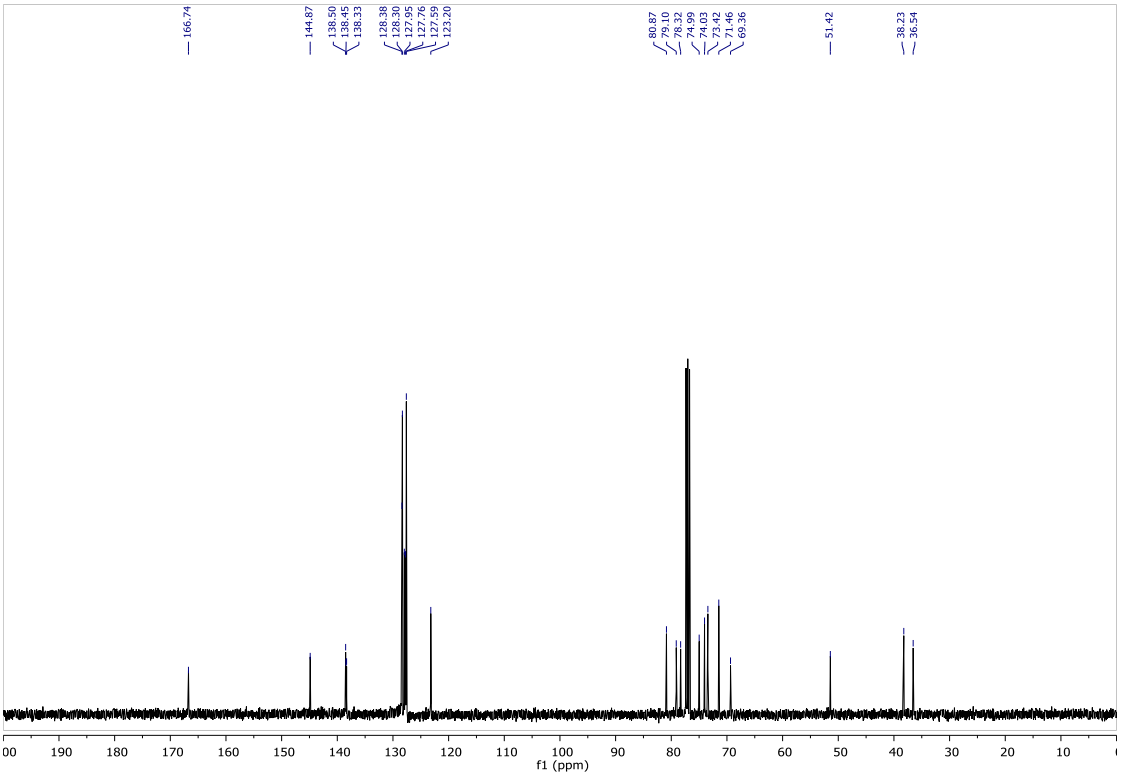

Noesy NMR (400 MHz, $CDCl_3$)



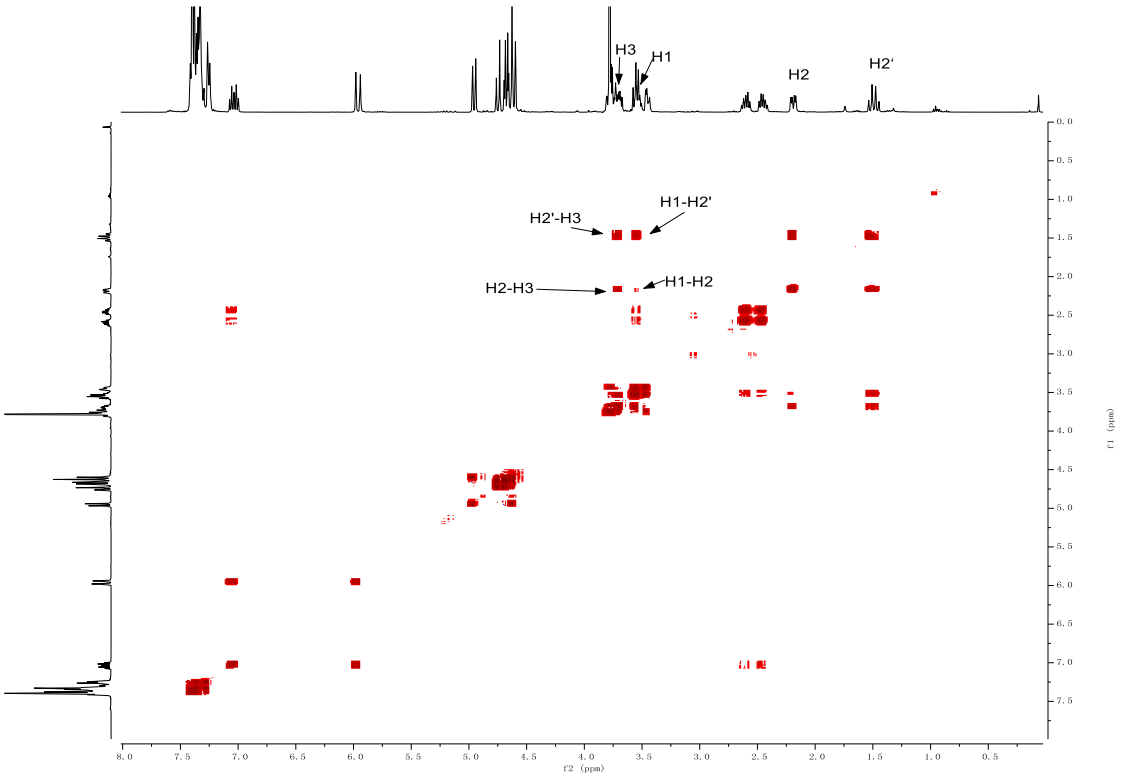
## Compound 4hα



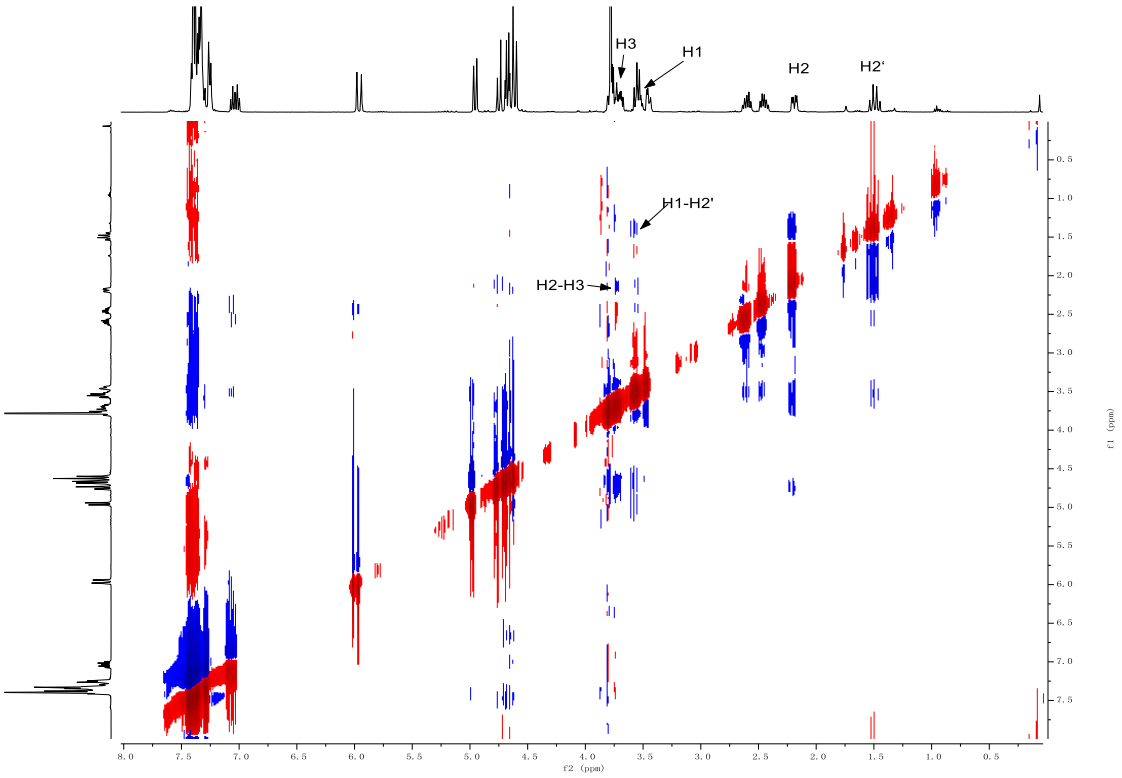

$^{13}$C NMR (100 MHz, $CDCl_3$)



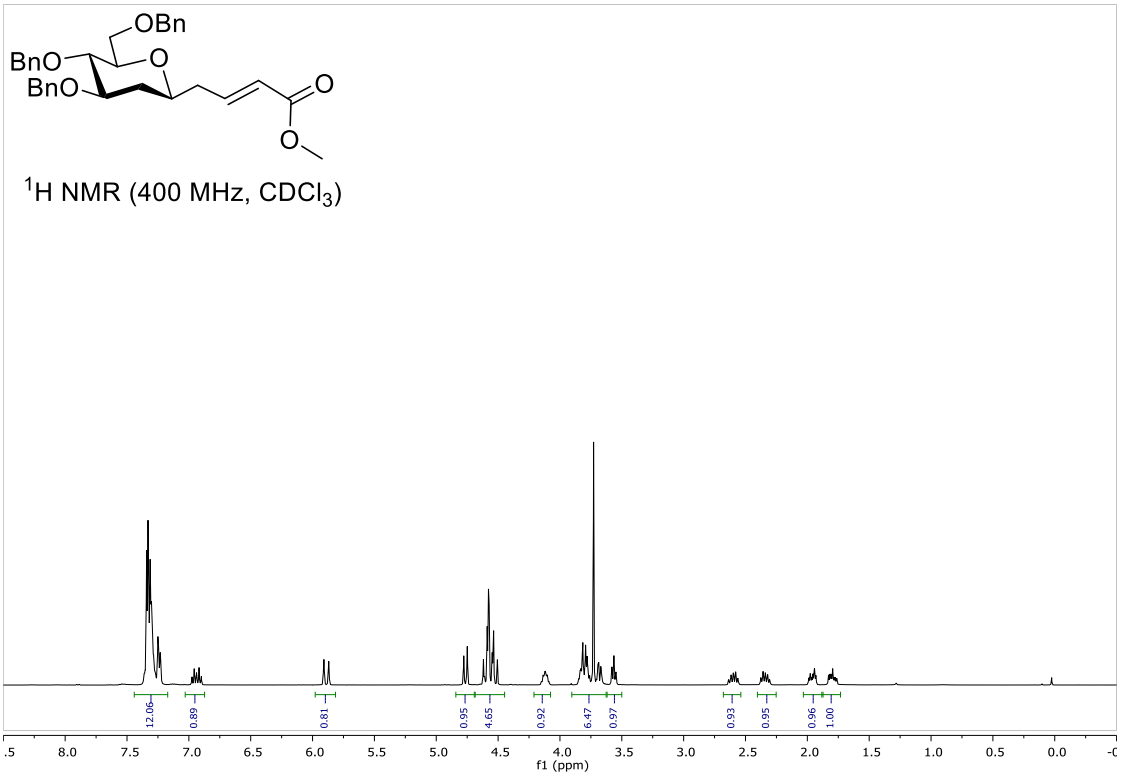
Gcosy NMR (400 MHz, $CDCl_3$)



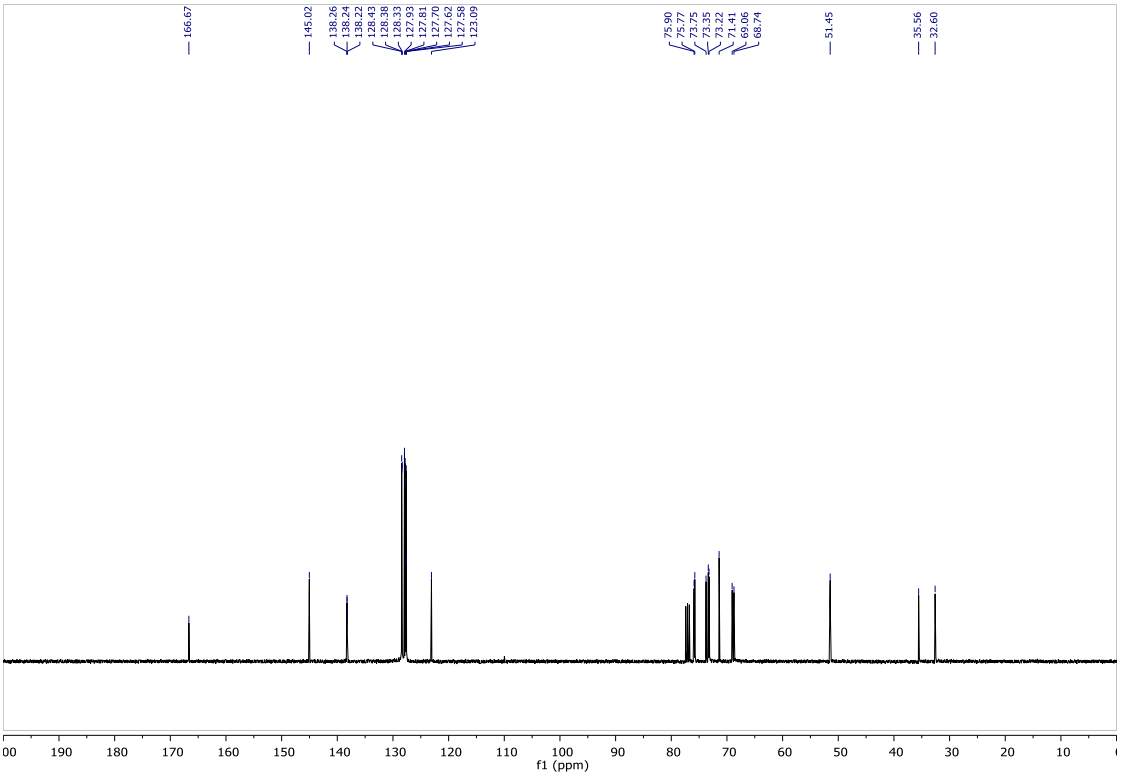

Noesy NMR (400 MHz, $CDCl_3$)



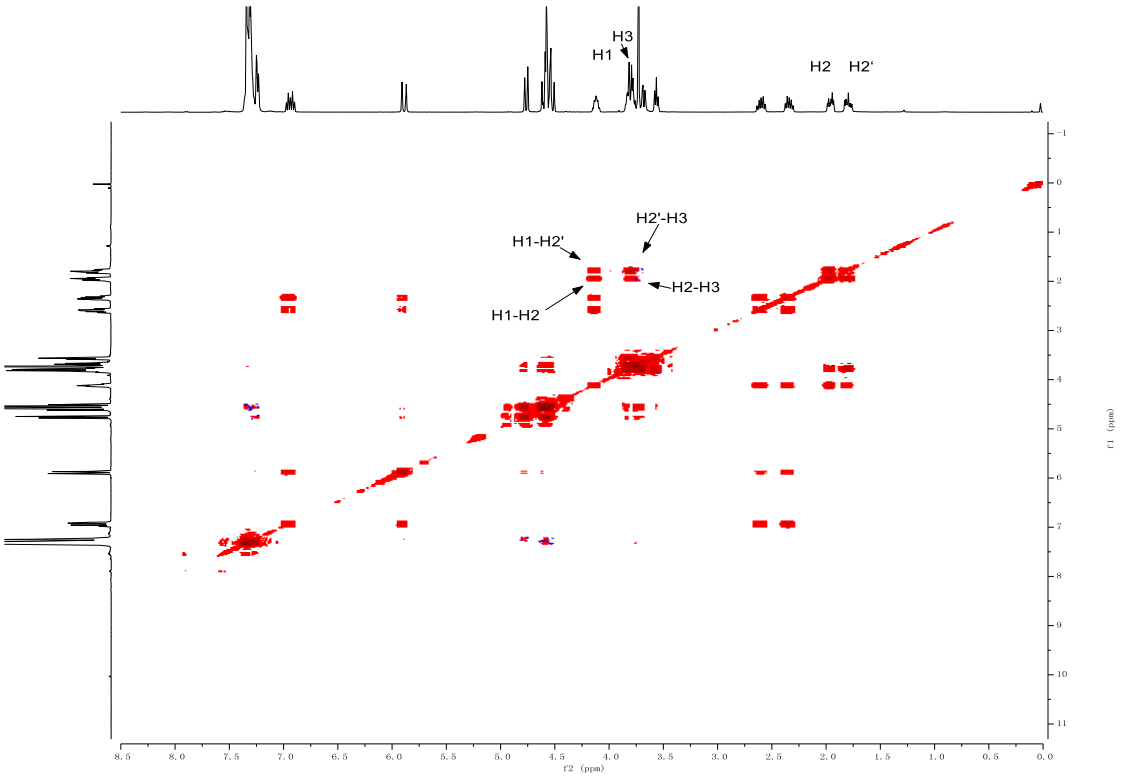
## Compound 4hβ



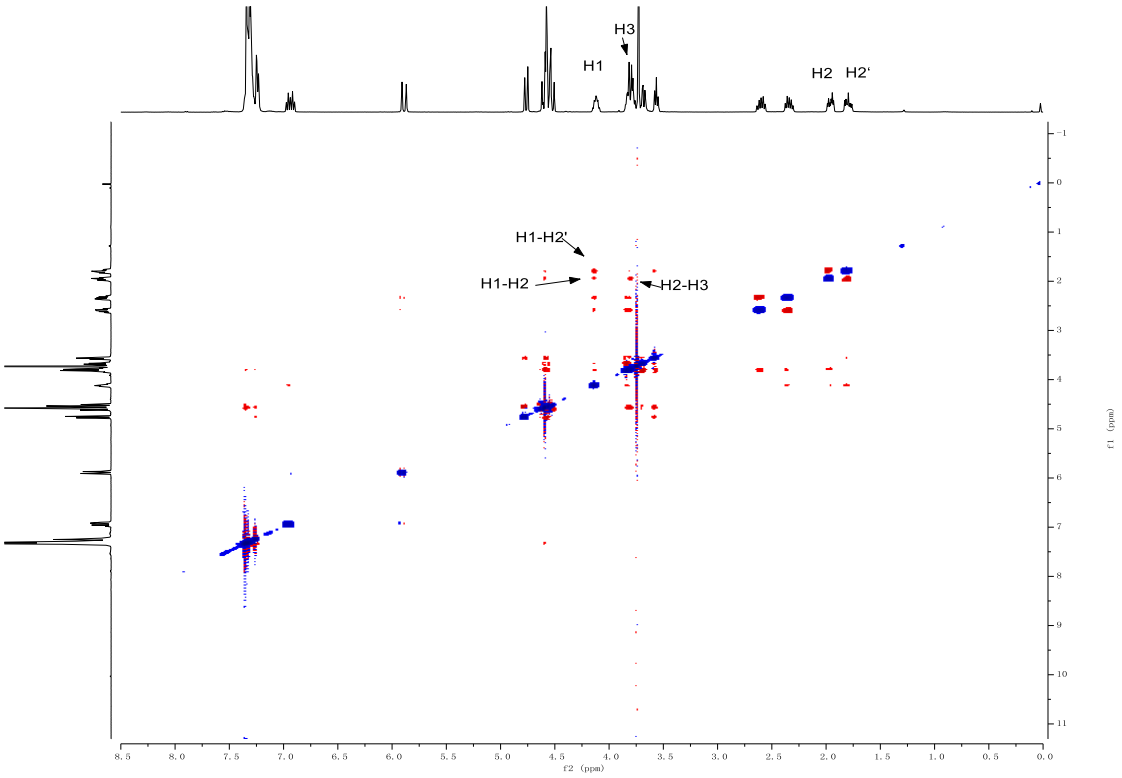

$^{13}$C NMR (100 MHz, CDCl$_3$)



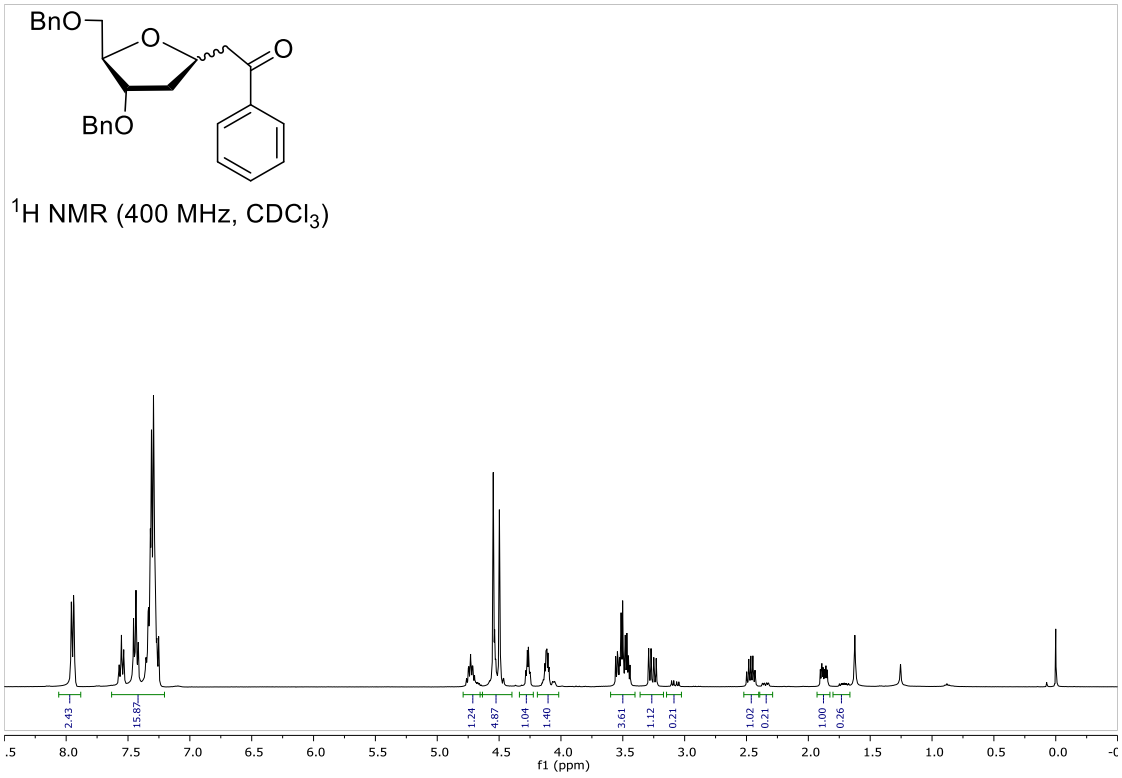
Gcosy NMR (400 MHz, $CDCl_3$)



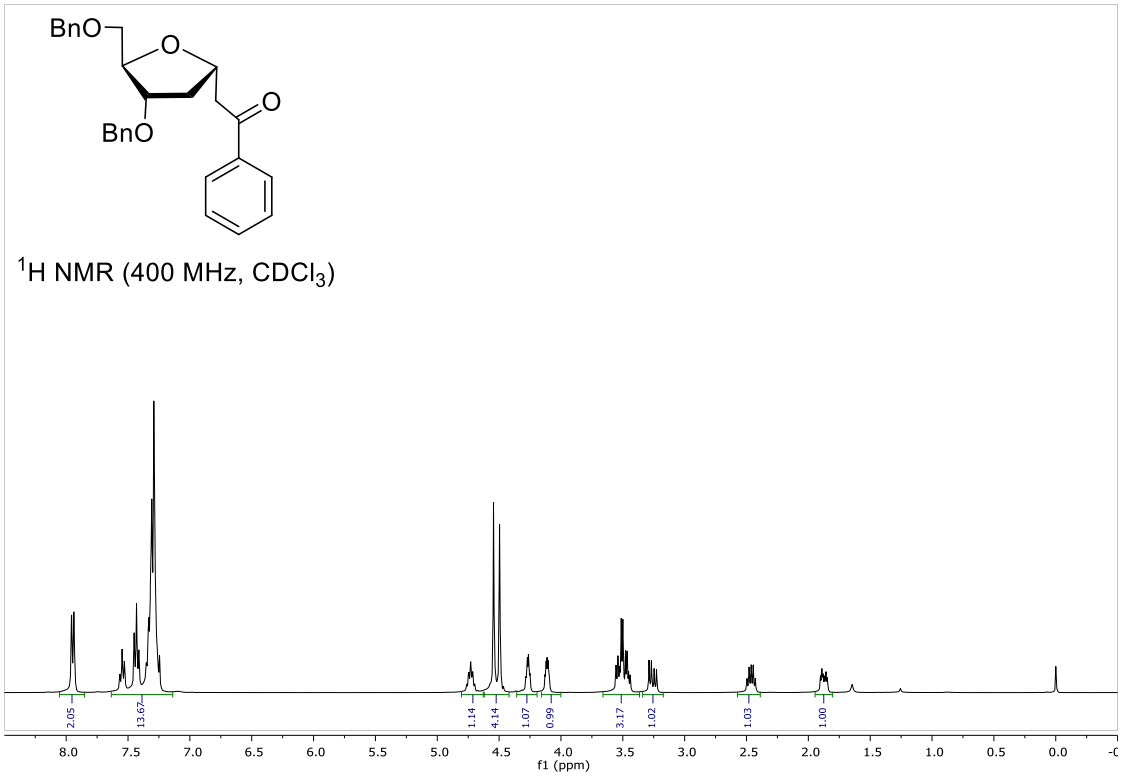

Noesy NMR (400 MHz, $CDCl_3$)



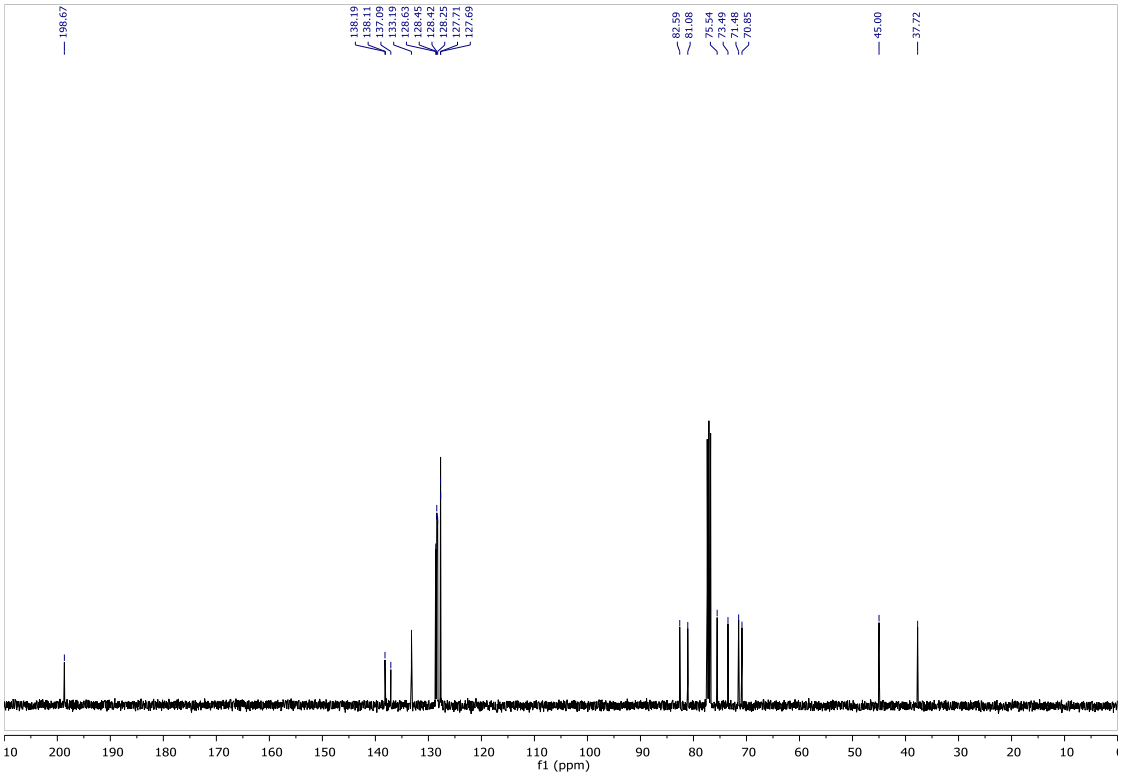
## Compound 4i (α/β = 6.2:1)



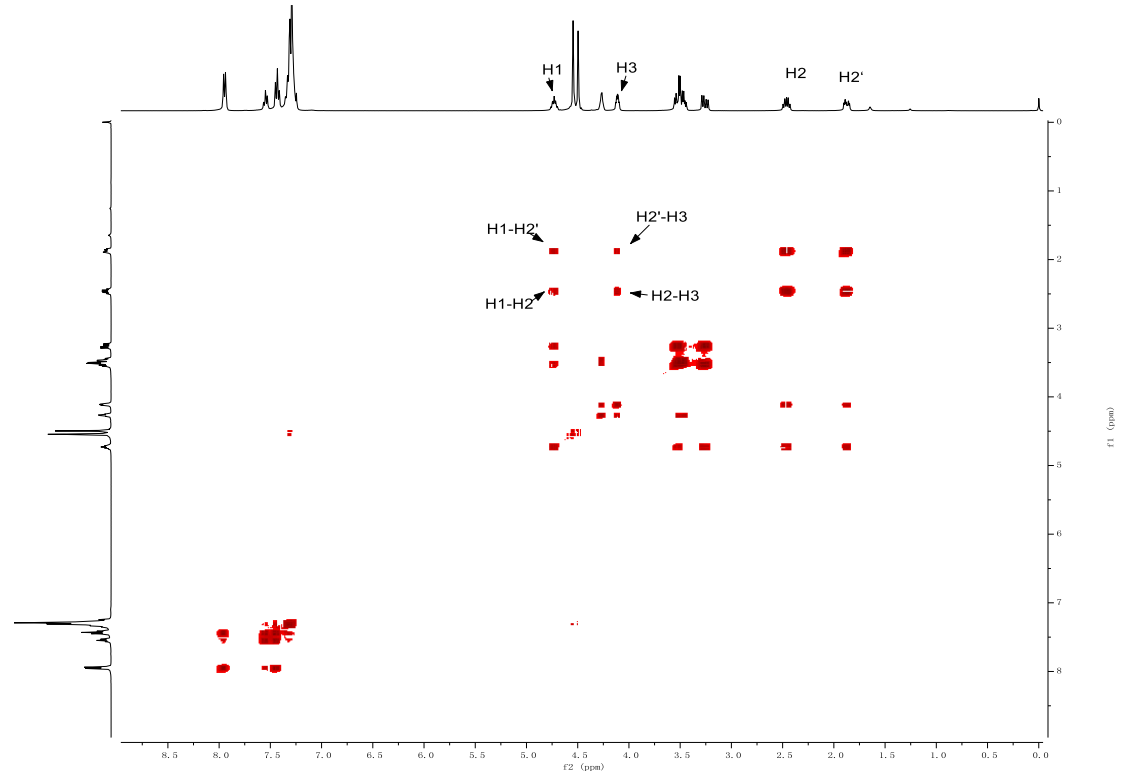

## Compound 4iα



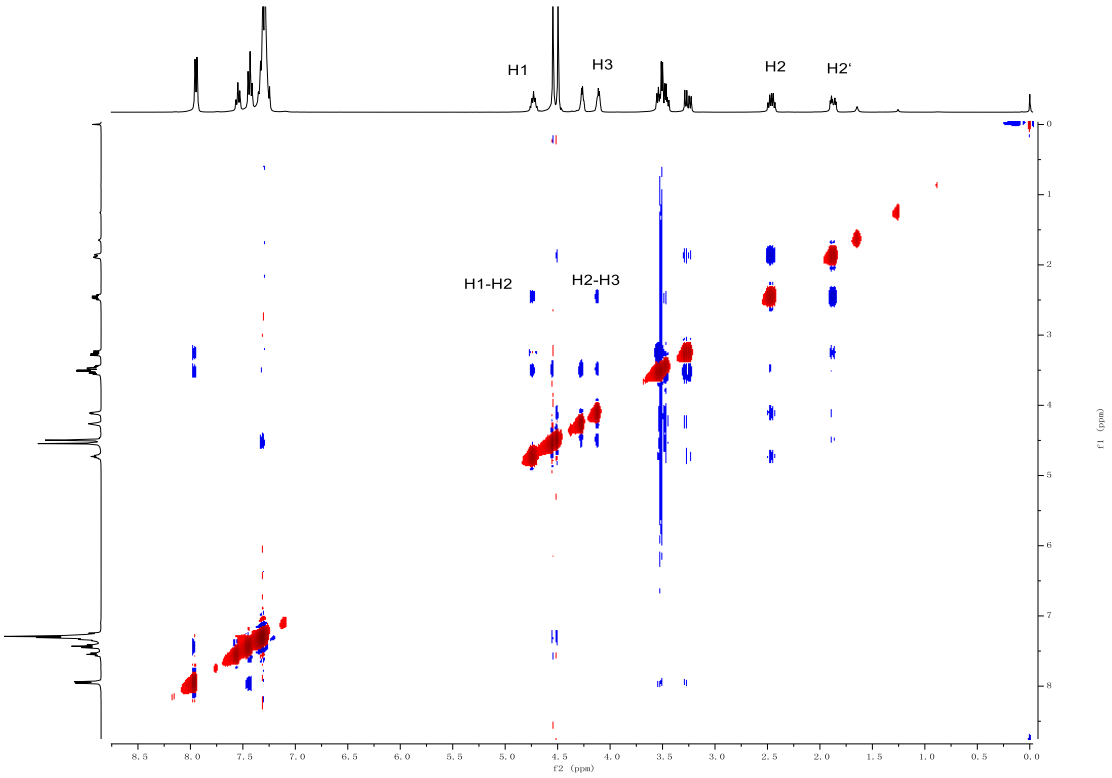
$^{13}C$ NMR (100 MHz, $CDCl_3$)



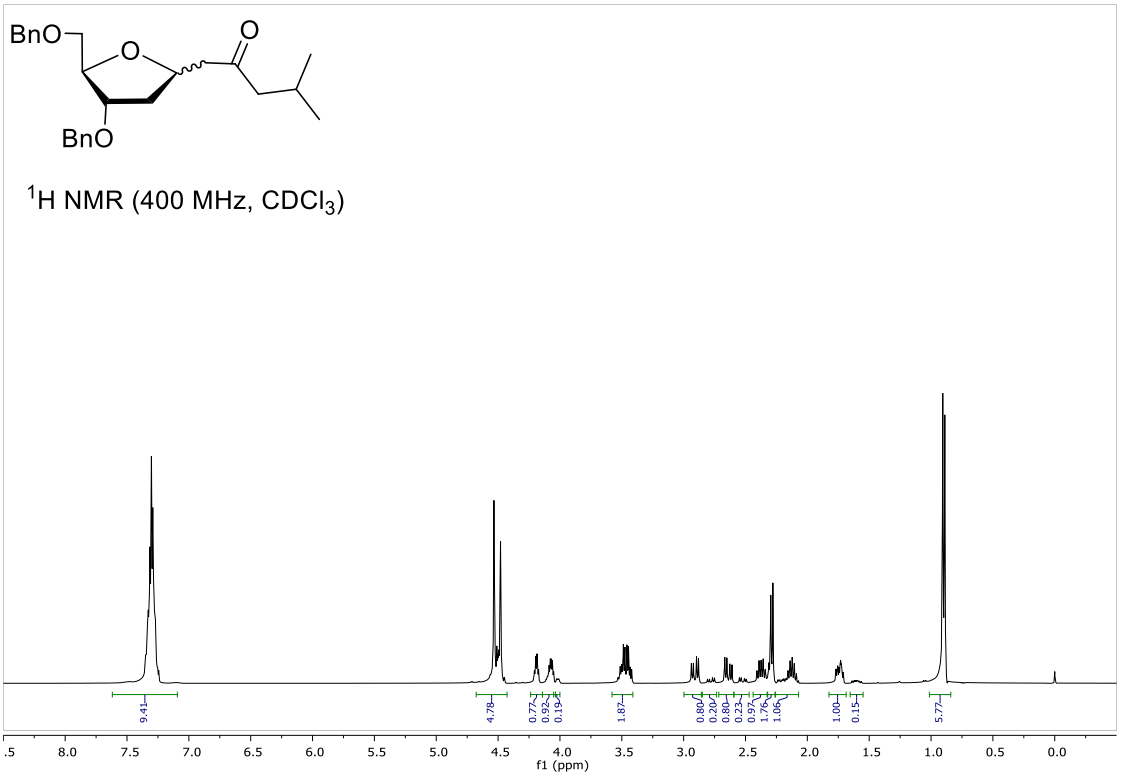

Gcosy NMR (400 MHz, $CDCl_3$)



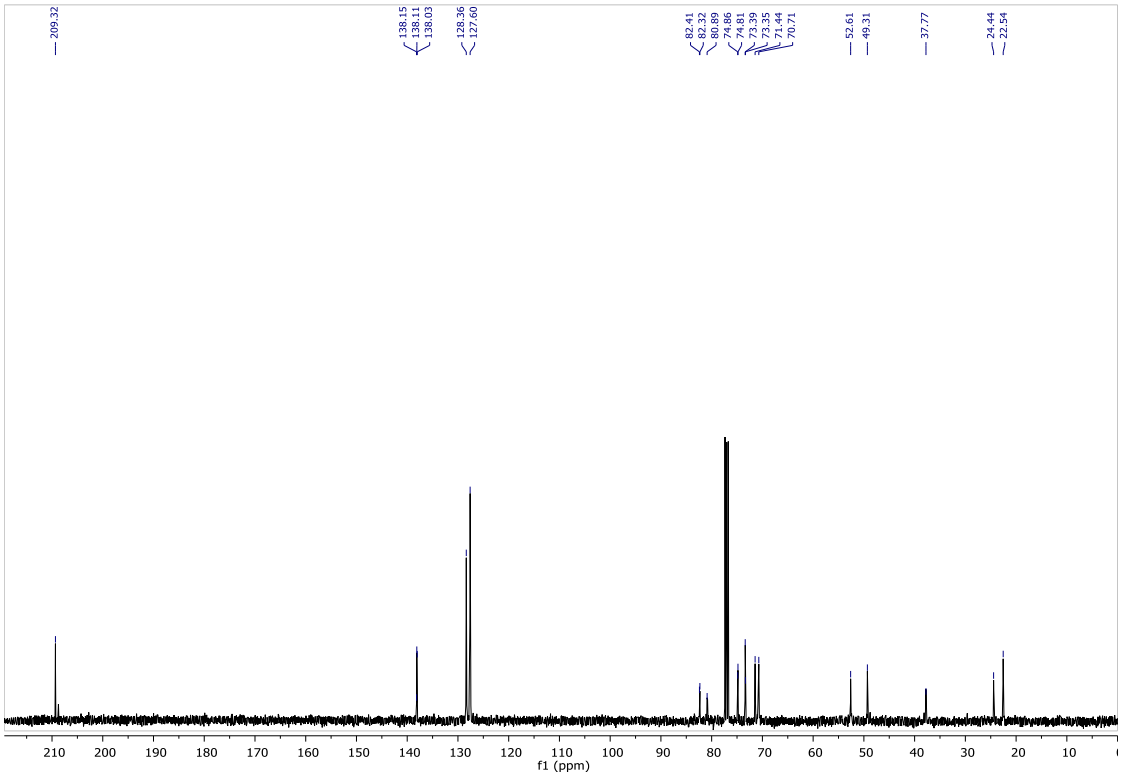
Noesy NMR (400 MHz, $CDCl_3$)



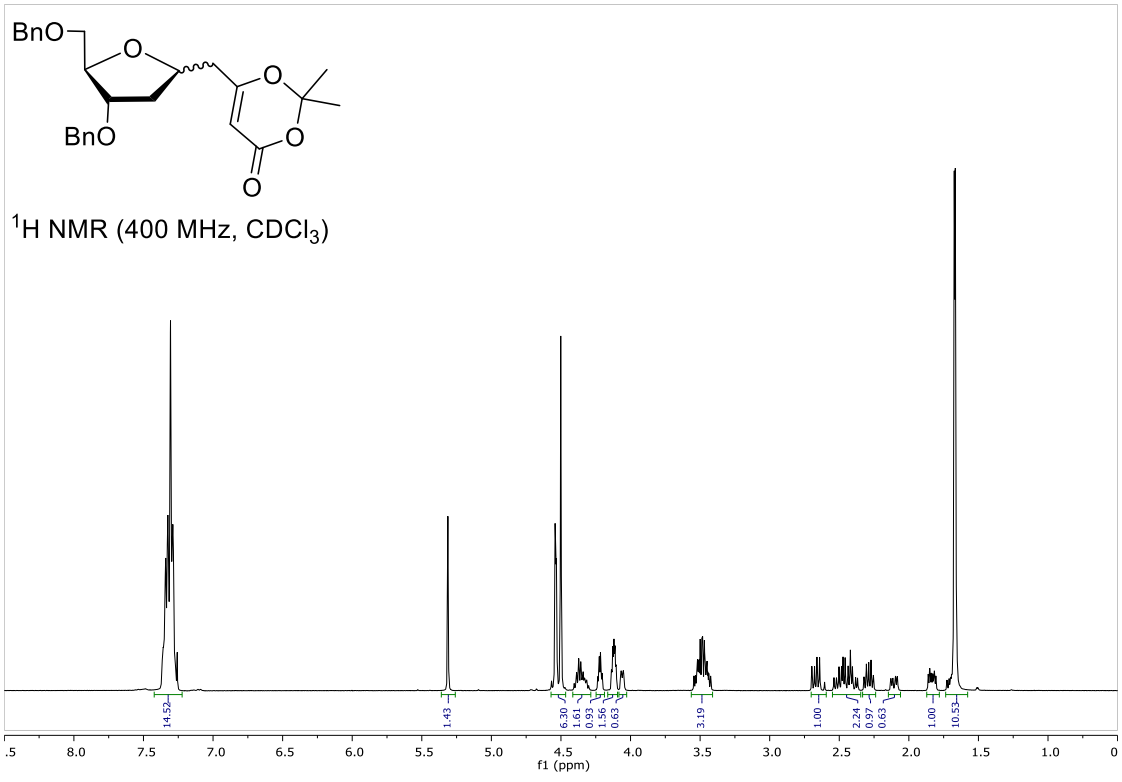

**Compound 4j (α/β = 3.5:1)**



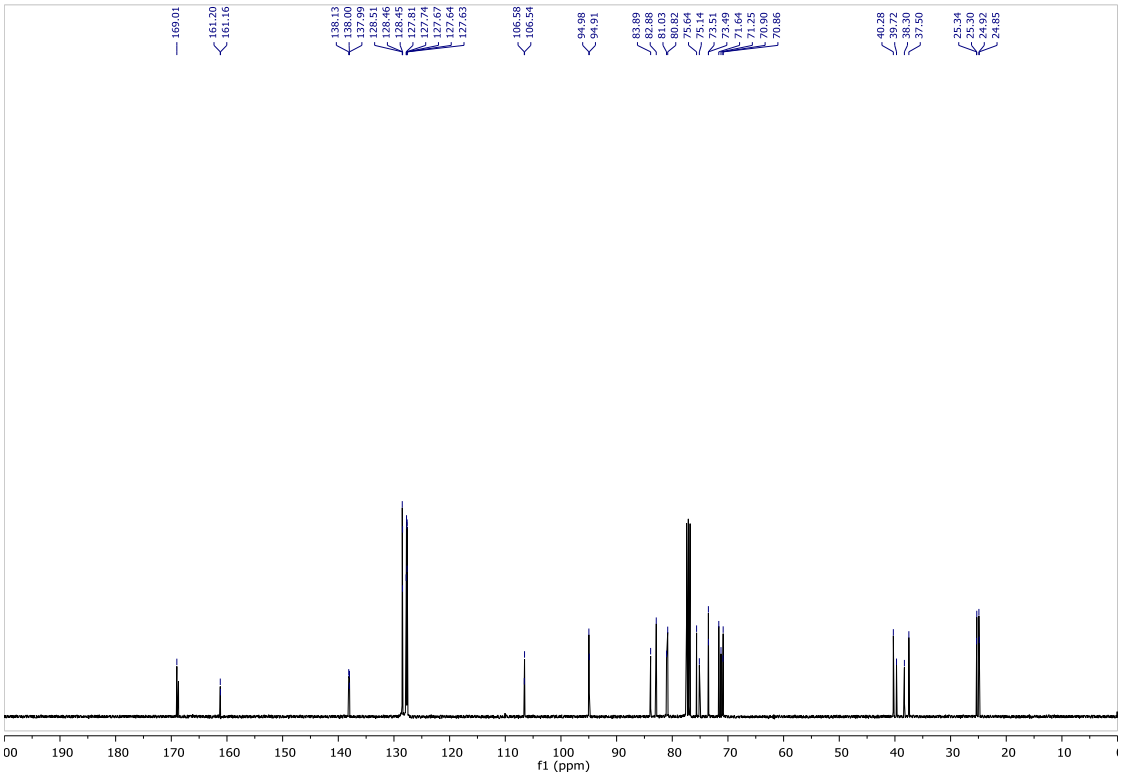
$^{13}C$ NMR (100 MHz, $CDCl_3$)



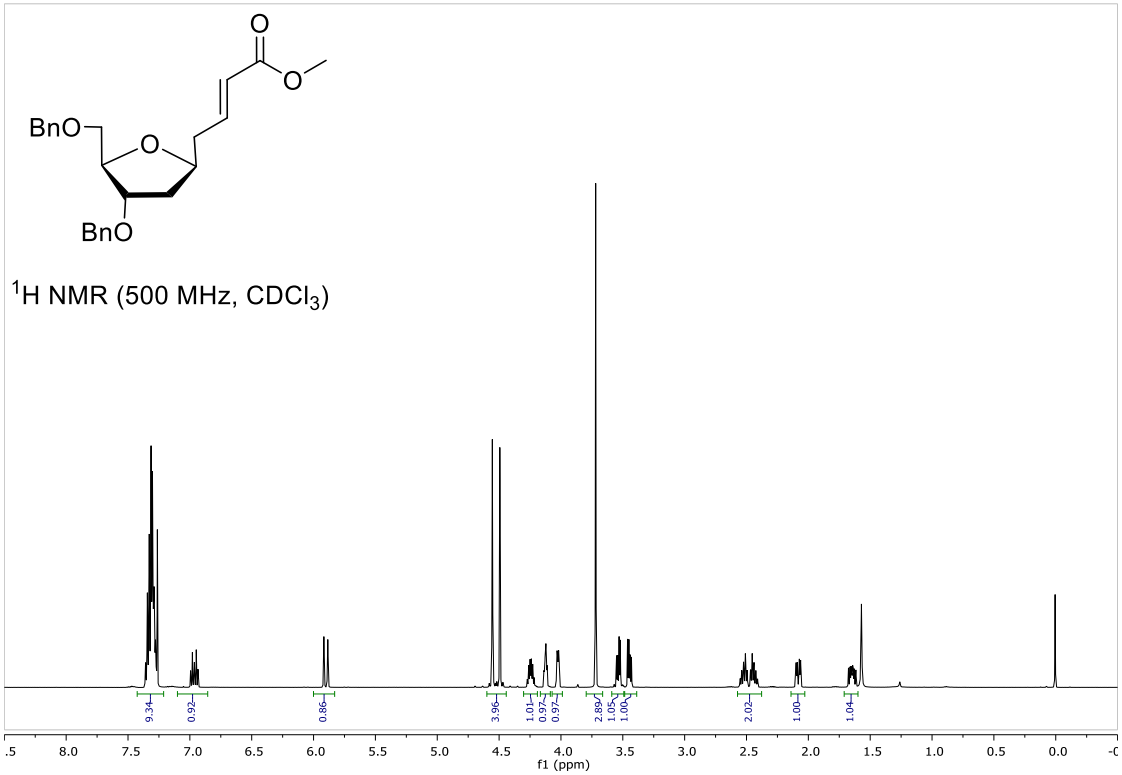

## Compound 4k (α/β = 1.5:1)



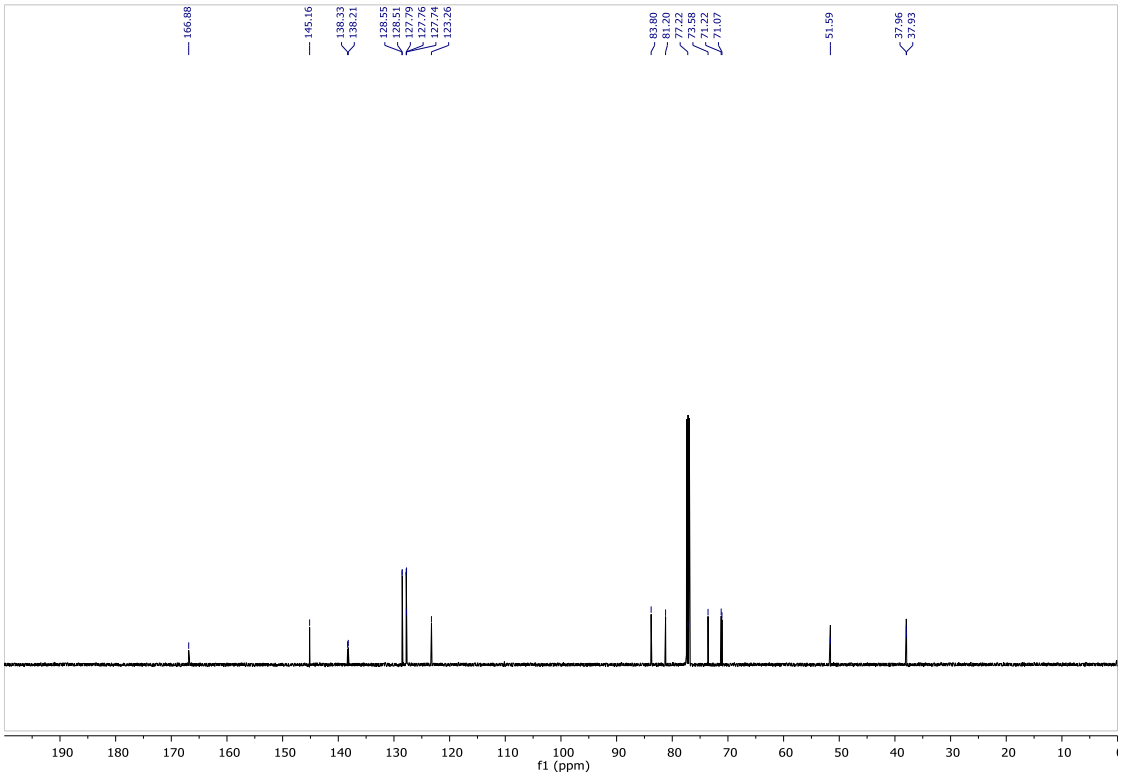
$^{13}$C NMR (100 MHz, $CDCl_3$)



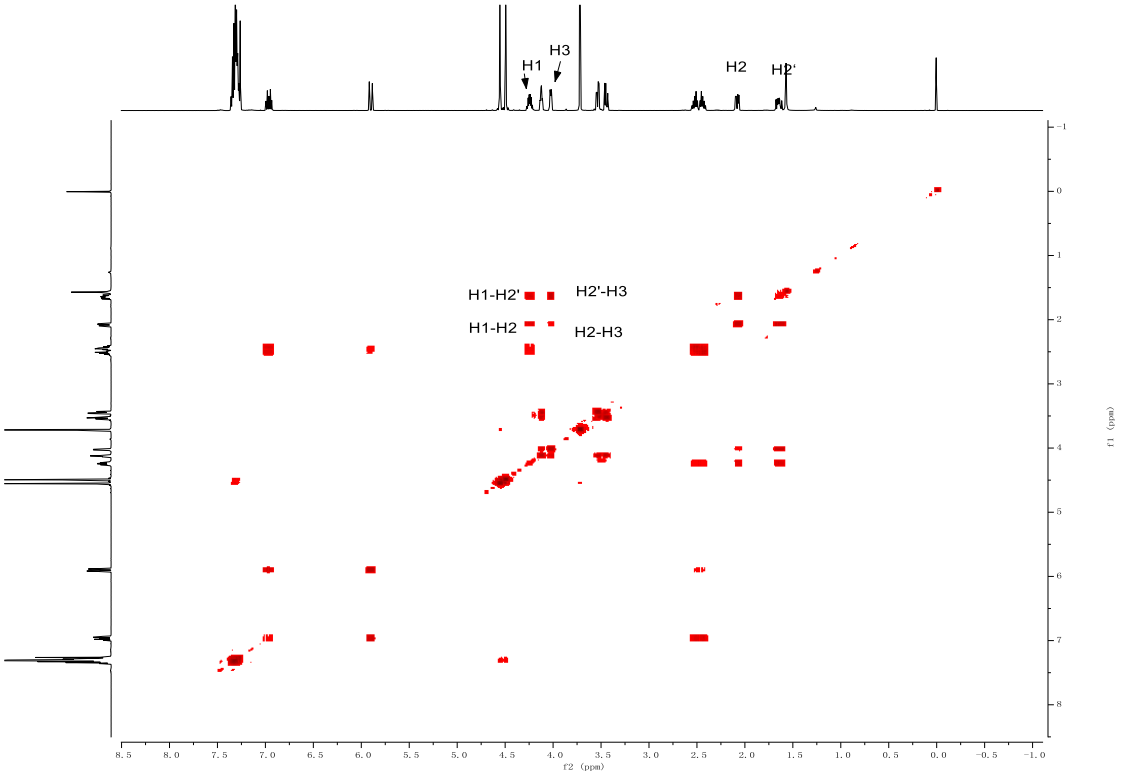

## Compound 4lβ



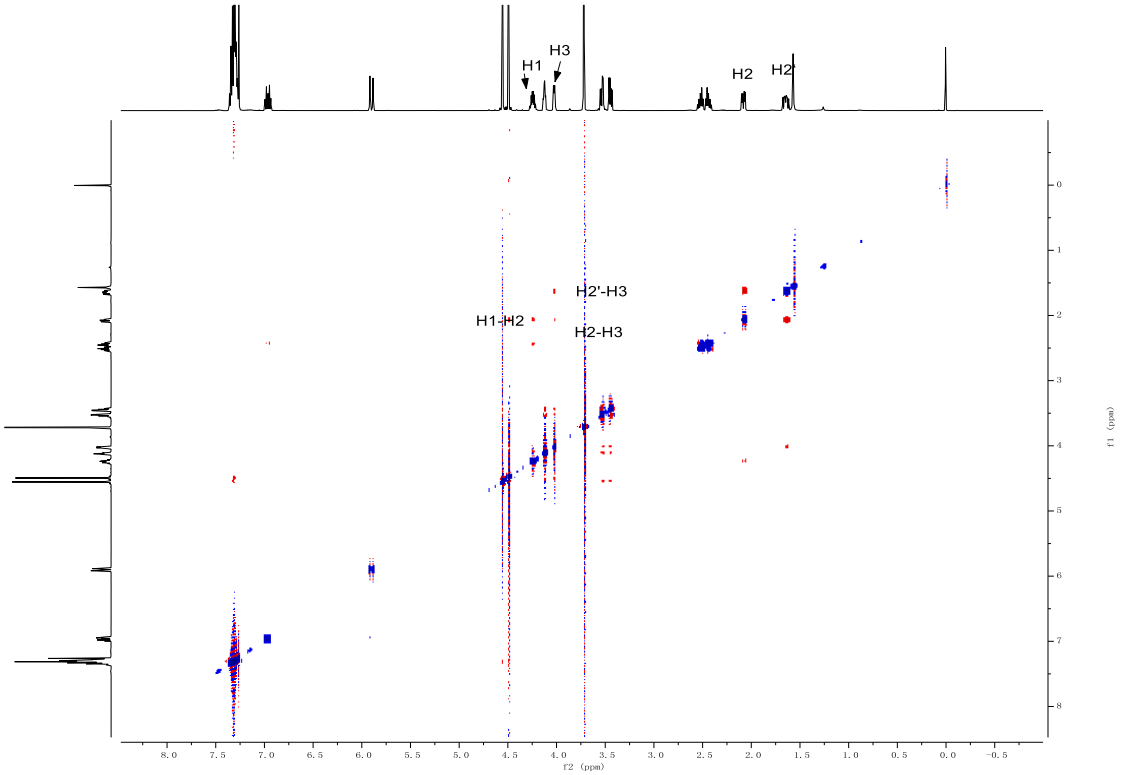
$^{13}C$ NMR (125 MHz, $CDCl_3$)



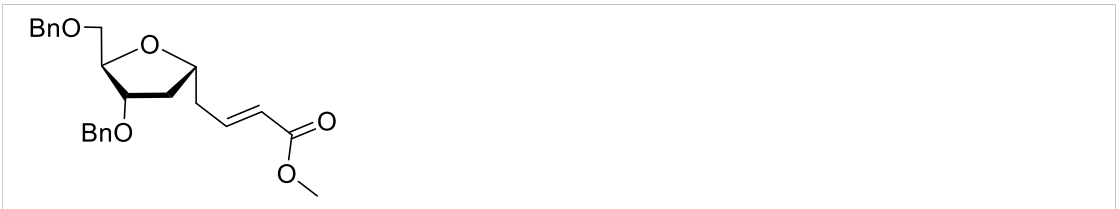

Gcosy NMR (500 MHz, $CDCl_3$)



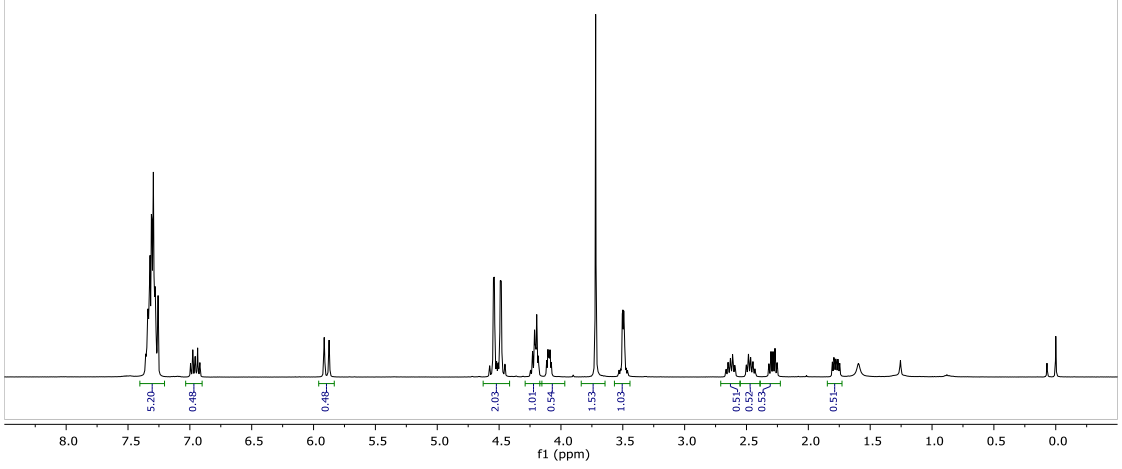
Noesy NMR (500 MHz, $CDCl_3$)



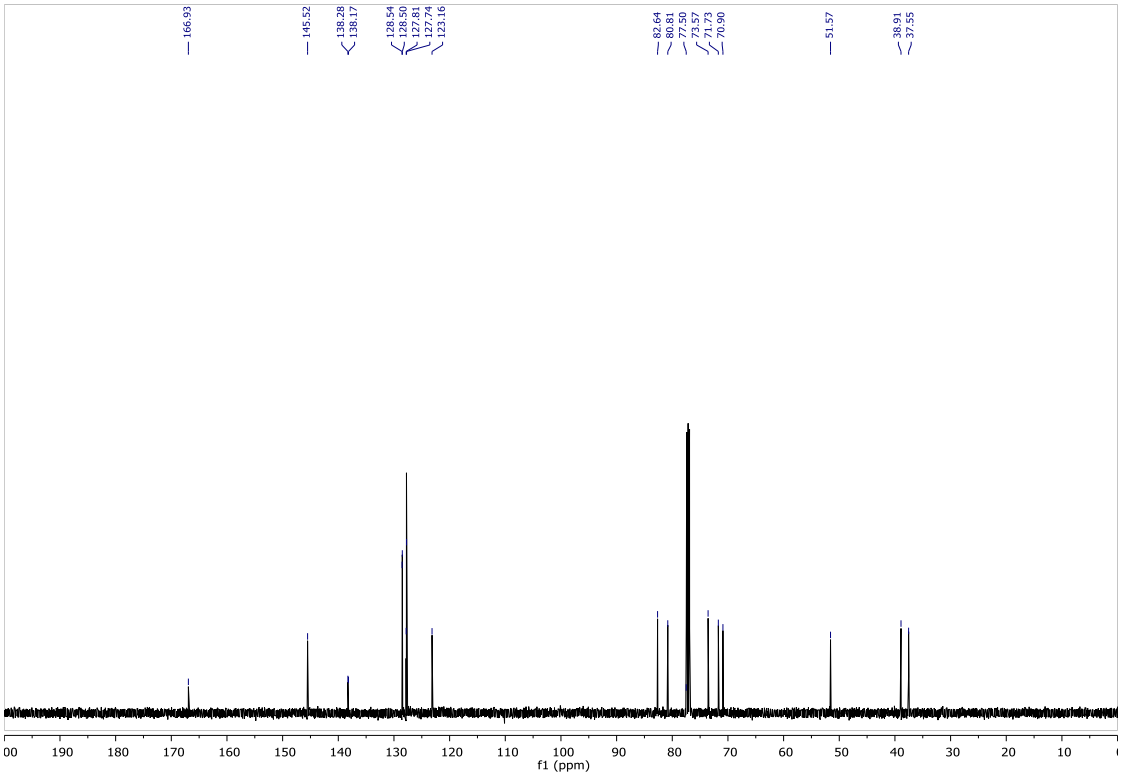

## Compound 4lα



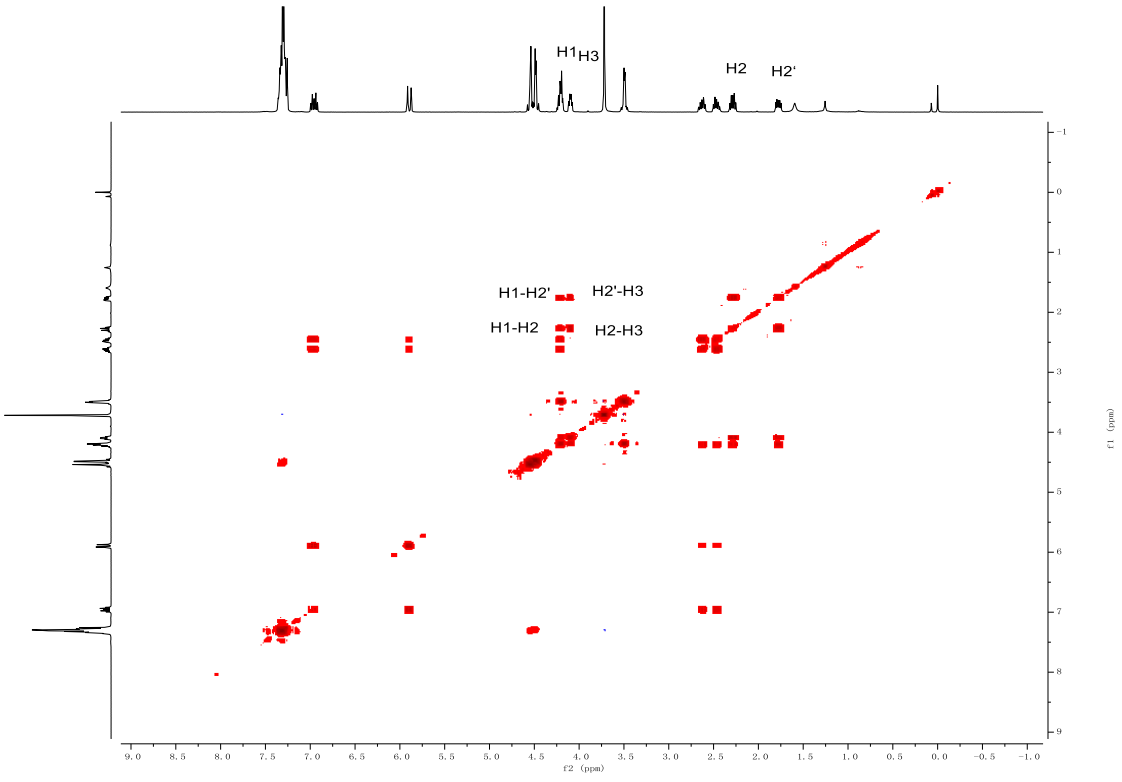

$^1$H NMR (500 MHz, $CDCl_3$)



$^{13}C$ NMR (125 MHz, $CDCl_3$)




Gcosy NMR (500 MHz, $CDCl_3$)



Noesy NMR (500 MHz, $CDCl_3$)